Driven self-assembly, part 1

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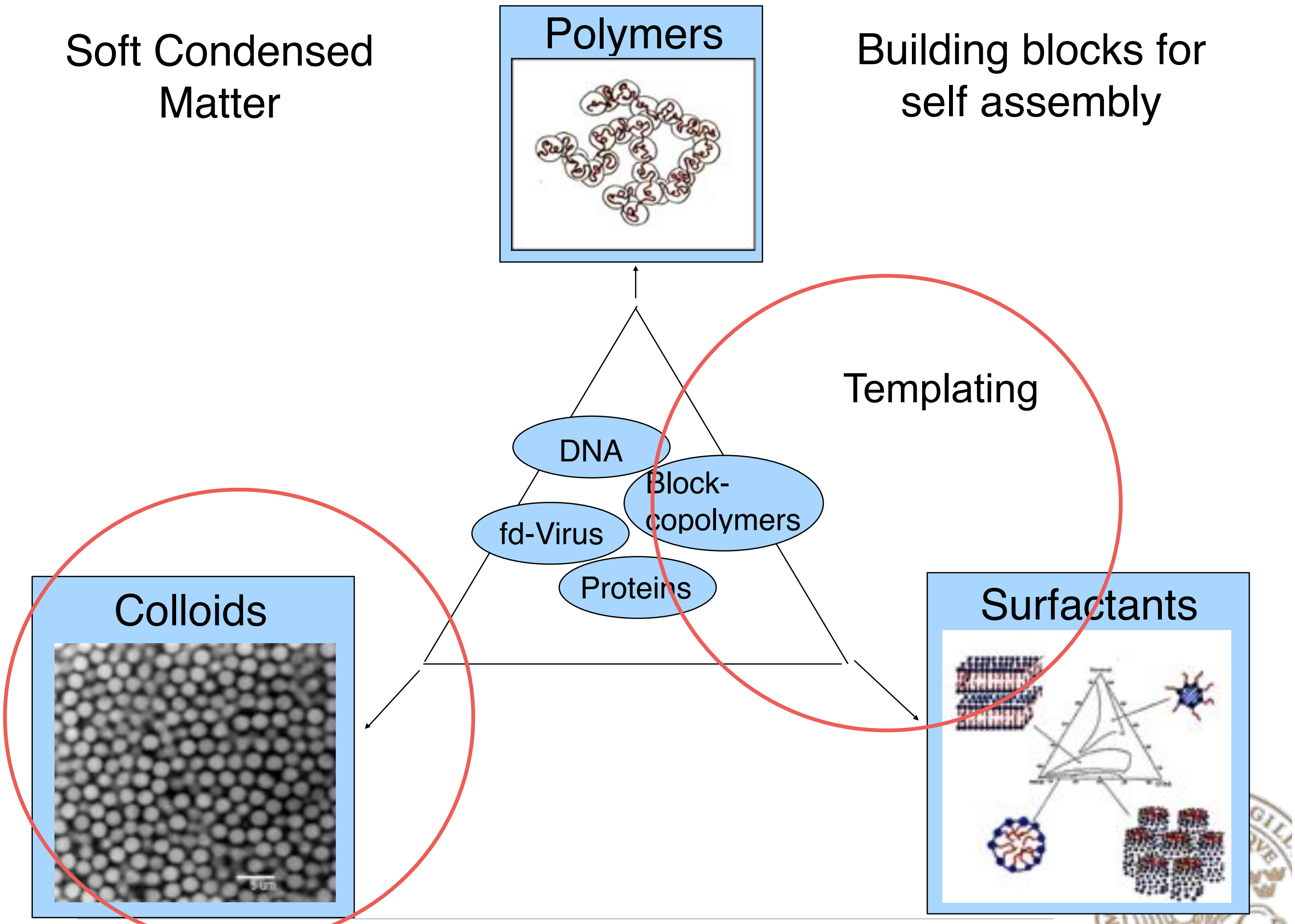
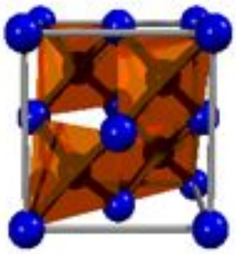
Soft Condensed Matter

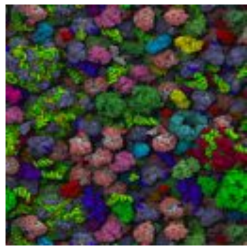
Building blocks for self assembly

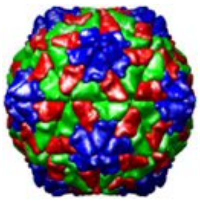


Self-assembly

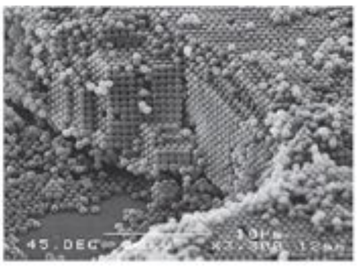


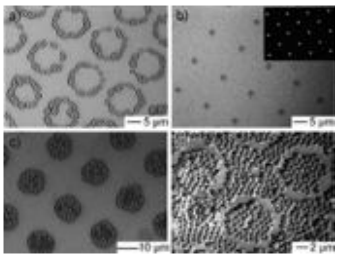
Nature does very well



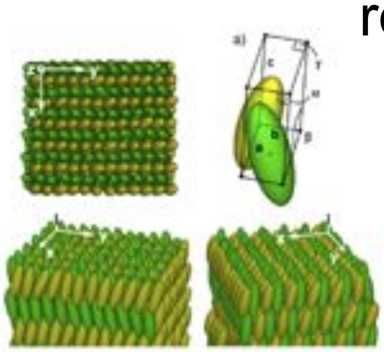


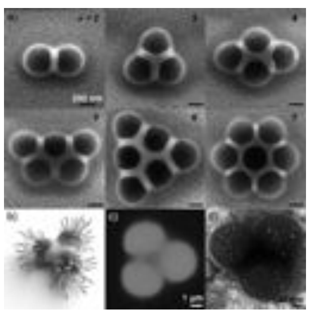
Self-assembly

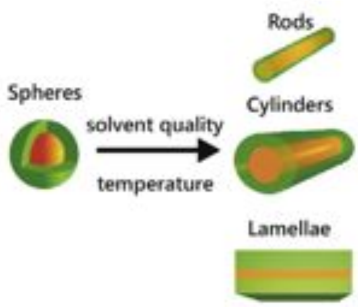




Scientists do reasonably well







Equilibrium self-assembly - where is the problem

System evolves to state with lowest
thermodynamic potential (G, H,…)

but…

- resulting assembled structures often irregular, polydisperse
- spherical colloids assemble only into dense ordered structures (fcc, bcc, hcp,…)

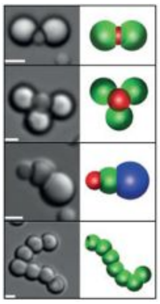
…

→ Directed Self-Assembly

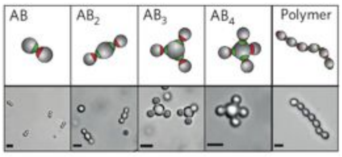
Directed self-assembly (DSA), an introduction

building blocks with
programmed instructions:
specificity, directionality,…

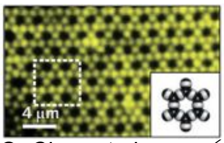
L. Cademartiri and K. J. M. Bishop, Nature Materials (2015)



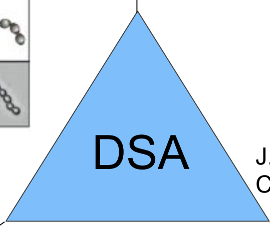
S. Sacanna et.al. Nature (2010)



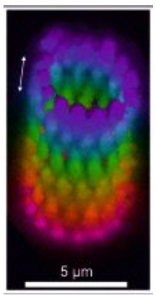
Y. Wang et al. Nature (2012)



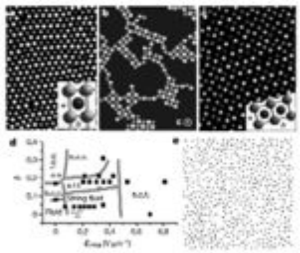
Q. Chen et al., Nature (2011)



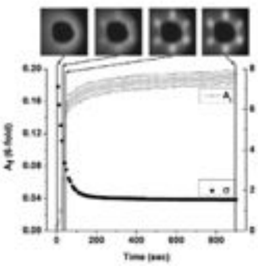
external fields driving SA



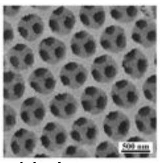
J. Crassous et al., Nature Comm. (2014)



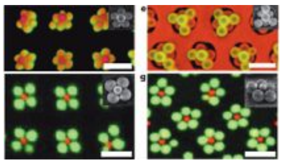
A. Yethiraj & A. van Blaaderen, Nature (2003)



J. McMullan & N. Wagner, J. Rheol. (2009)

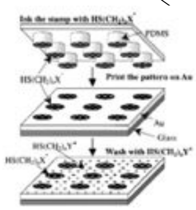


Wang & Möhwald, J. Mater. Chem. (2004)



A. Demirörs et.al. Nature (2013)

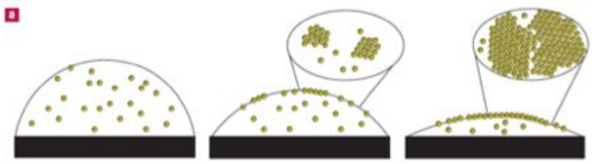
use of templates



J. Aizenberg et al., Phys Rev Lett (2000)

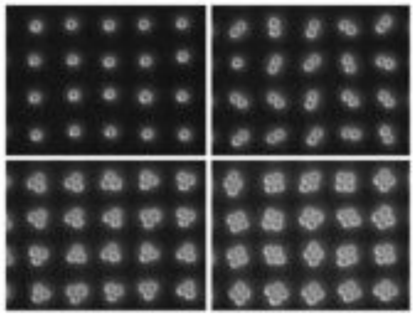
Template-directed or driven SA

Interface driven self-assembly

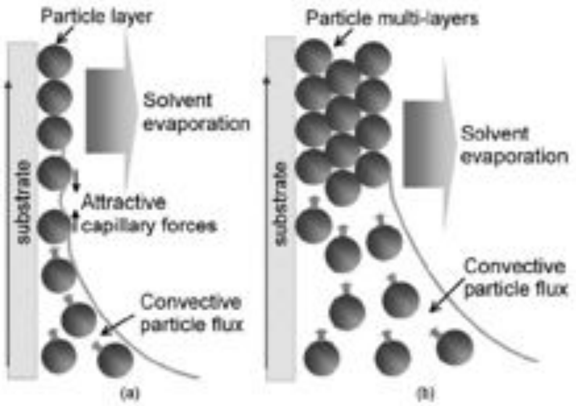


T. Bigioni et al., Nature Materials (2006)

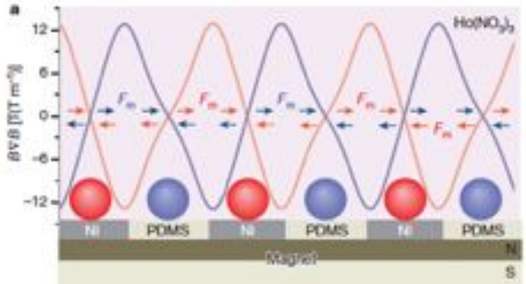
Chemical patterns



I. Lee et al., Adv. Mat. (2002)



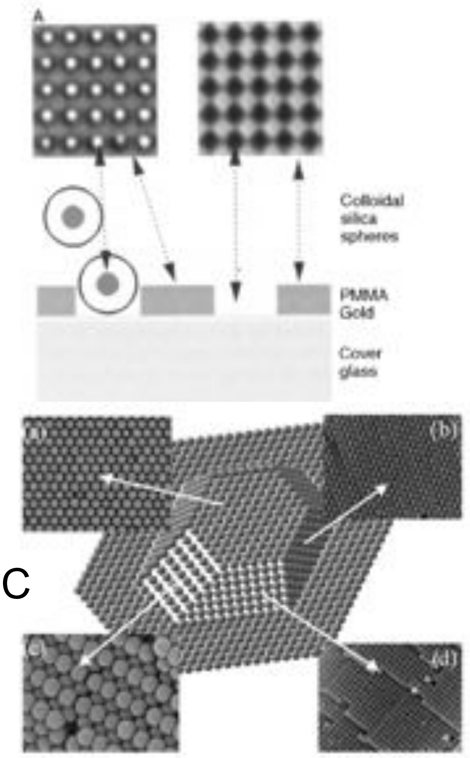
Field gradient driven self-assembly



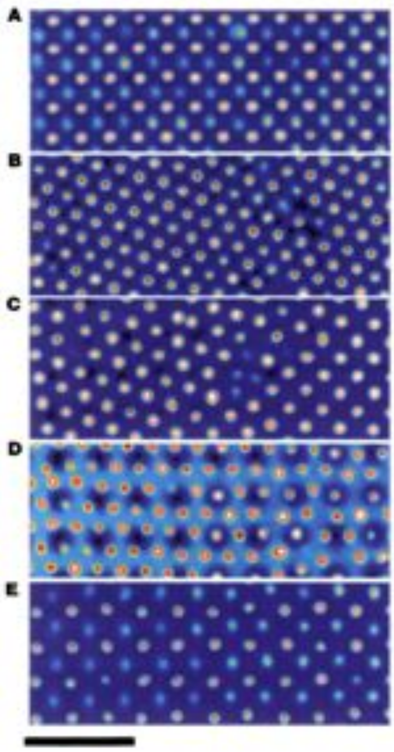
A. Demirörs et.al. Nature (2013)

N. V. Dziomkina and G. J. Vancso, Soft Matter (2005)

Template-directed crystal growth



FCC



N. V. Dziomkina and G. J. Vancso, Soft Matter (2005)

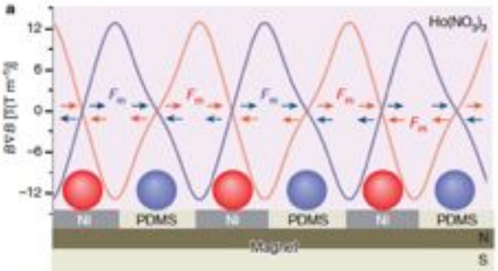
A. van Blaaderen et al. Nature (1997)

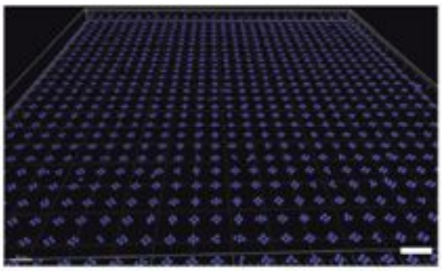
Using magnetic moulds to assemble colloids

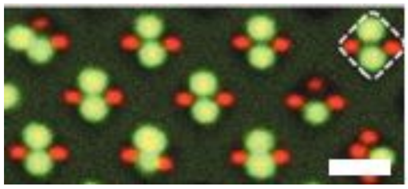
$$F_{\mathrm{m}} = -\nabla U_{\mathrm{m}}$$

sensitive to material → selective forces

$$U_M(\boldsymbol{r}) = -2\pi a^3 \mu_0 \frac{\chi_{\mathrm{part}} - \chi_{\mathrm{sol}}}{\chi_{\mathrm{part}} + 2\chi_{\mathrm{sol}} + 3} |\boldsymbol{H}(\boldsymbol{r})|^2$$







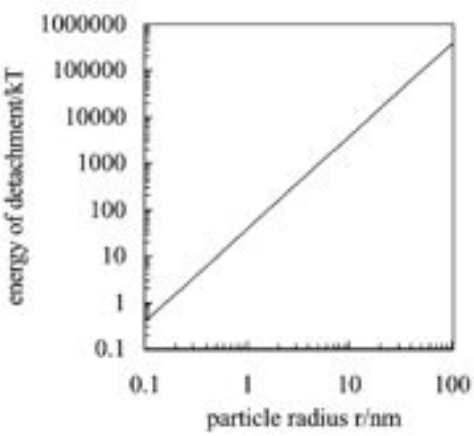
A. Demirörs et.al. Nature (2013)

Confining particles at interfaces

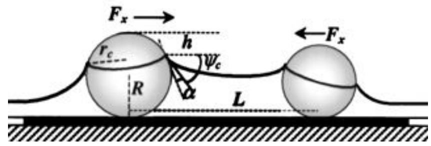
two main contributions:

reduction in interfacial energy
(Pickering emulsions)

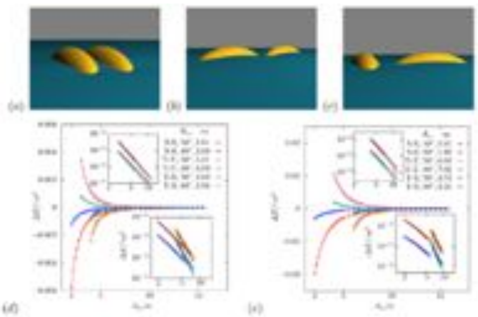
$$E = \gamma \pi {r_p}^2 (1 - |cos(\theta)|)^2$$



lateral capillary interactions



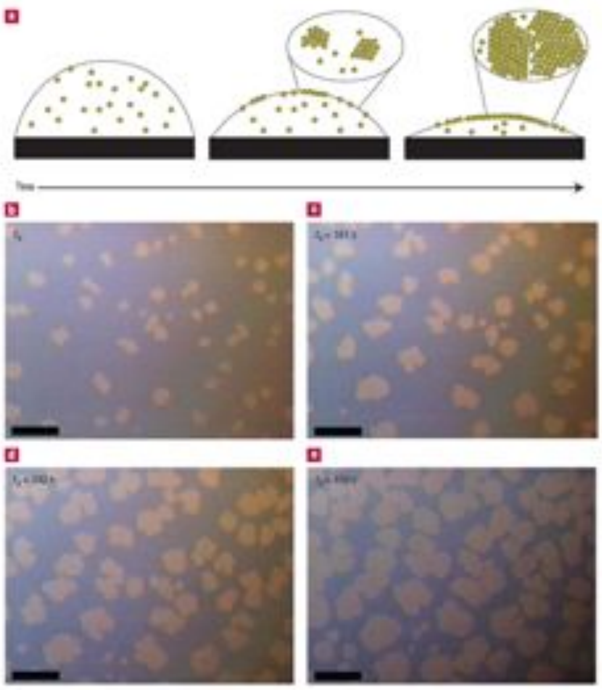
long range
shape dependent

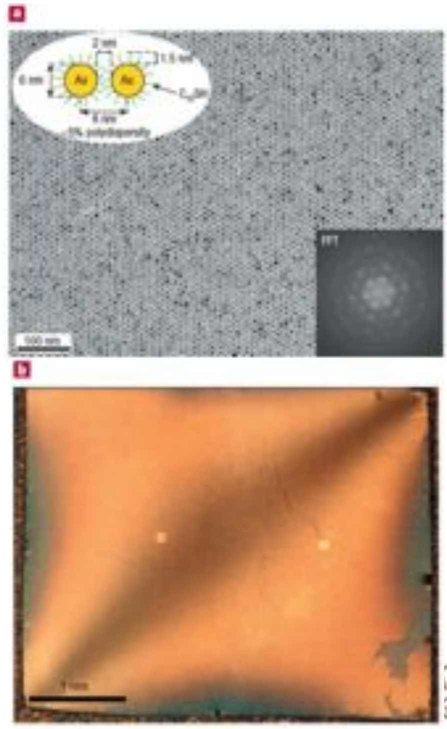


B. Binks, COCIS (2002)

Dasgupta et al., Langmuir (2014)

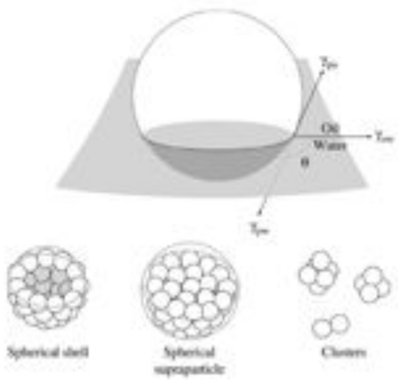
Interface-driven monolayer self-assembly

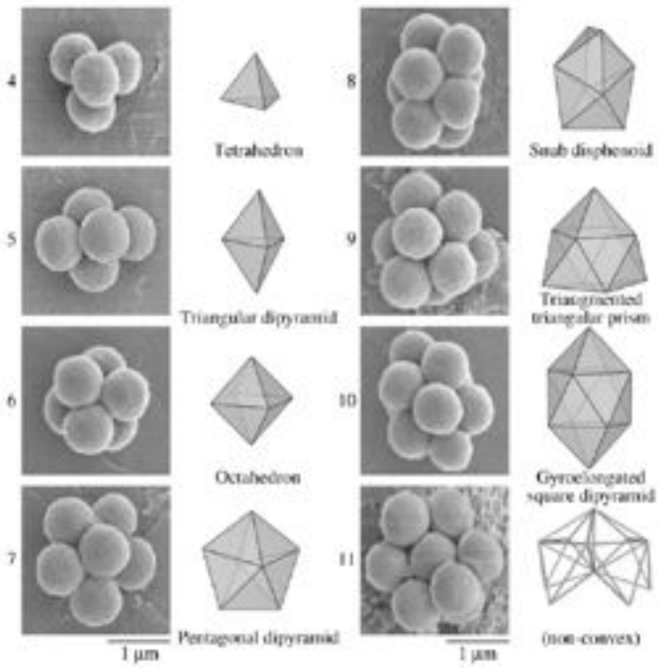




T. Bigioni et al., Nature Materials (2006)

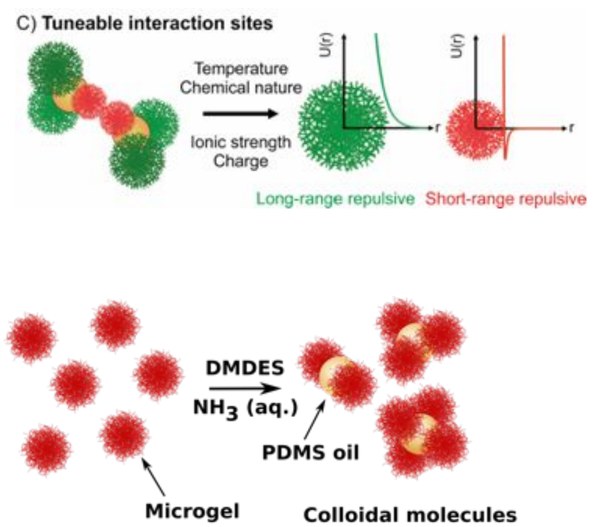
Interface-driven colloidal assemblies

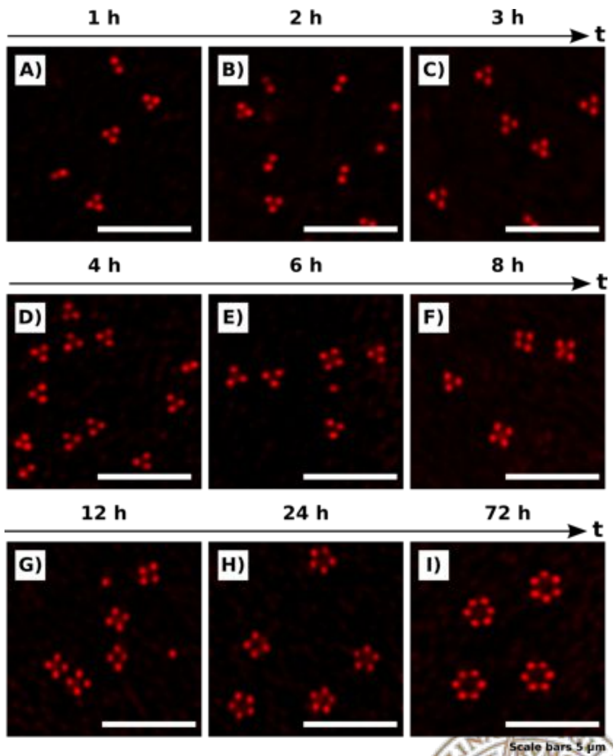




V. Manoharan, Solid State Comm. (2006)

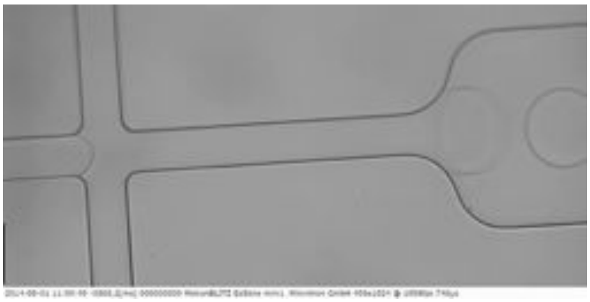
Building colloidal molecules through interface-driven SA



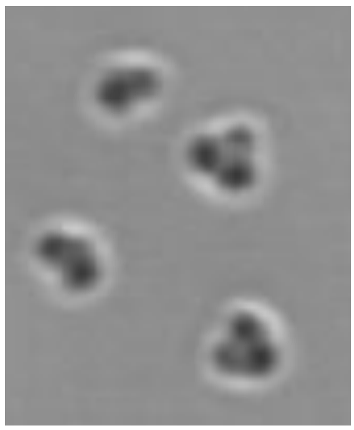


L. Månsson et al., Faraday Discussions (2015)

Building colloidal molecules through interface-driven SA



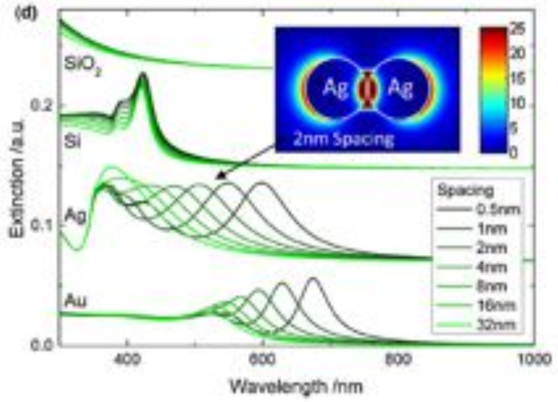
Controlled assembly via microfluidics devices



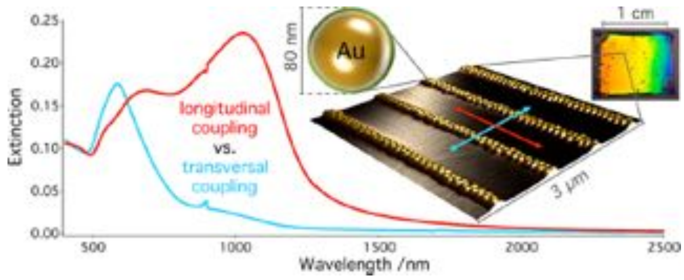
L. Månsson et al., Faraday Discussions (2015)

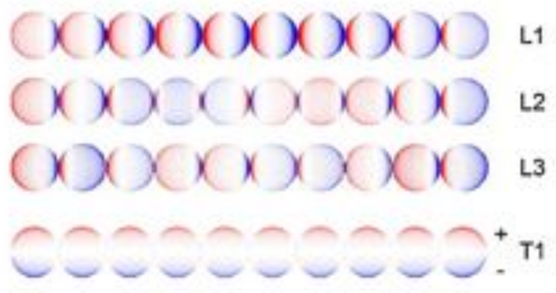
Nanoparticle assemblies for plasmonic applications

Very large fields



strong resonances in particle chains

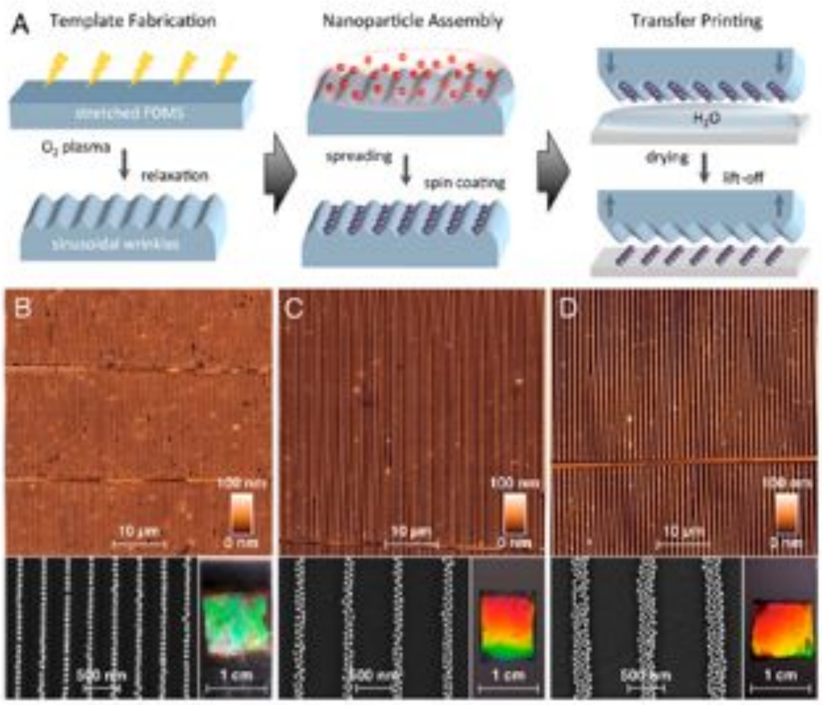




need large arrays
perfect control of particle distance
easy to fabricate
low defect numbers

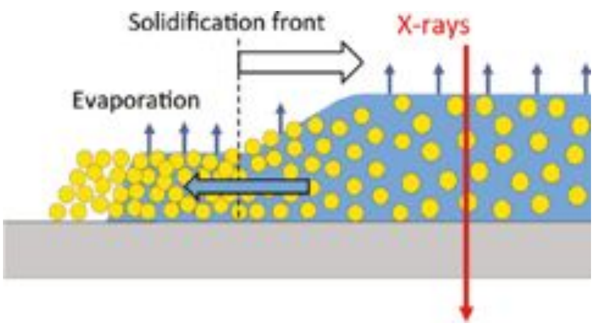
Karg et al., Materials Today (2015)

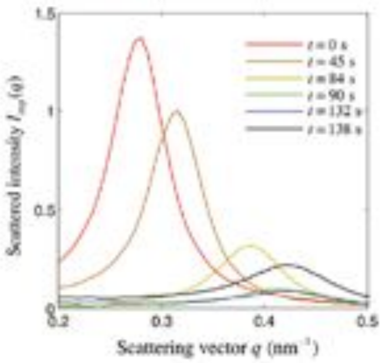
Templates for SA of large-scale plasmonic structures



Schweikart & Fery, Microchim. Acta (2009)
C. Lu et al., Soft Matter (2007)
Hanske et al., Nano Letters (2014)

Drying front driven - fast track to phase diagrams





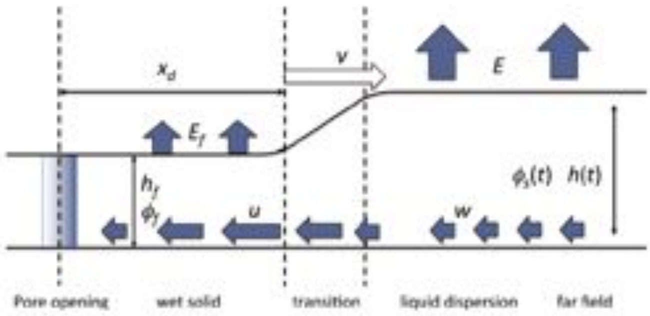
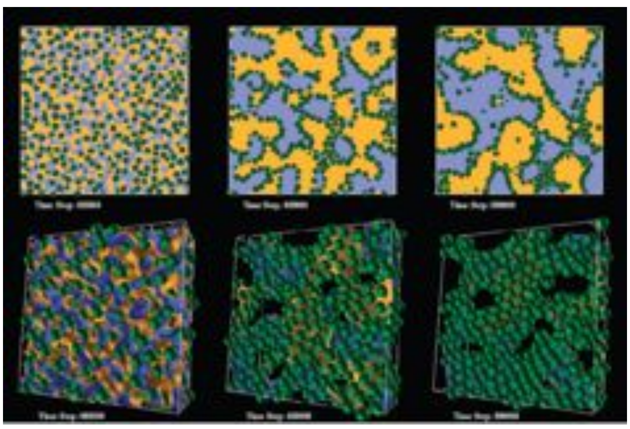


Figure 11. Sketch of the drying dynamics of a thin colloidal film. As a liquid, the film thickness h and solid volume fraction ϕ_s evolve with time, reaching final values h_f and ϕ_f, respectively, after aggregation. Evaporation over the dispersion, at a rate E, and the wet solid region, at a rate E_f, drives flow in the film. This can generate a far-field velocity w, a dispersant velocity u, and a front velocity v, of the aggregation and pore opening fronts.

J. Li et al., Langmuir (2011)

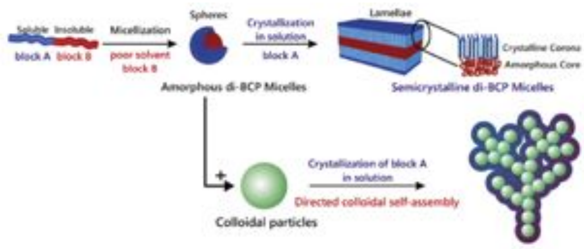
Temporarily evolving templates

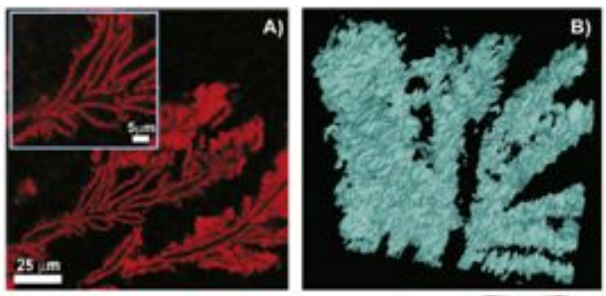
BIJEL: bicontinuous interfacially jammed emulsion gel



K. Stratford et al., Science (2005)

Surfactant or blockcopolymer mesophases as templates



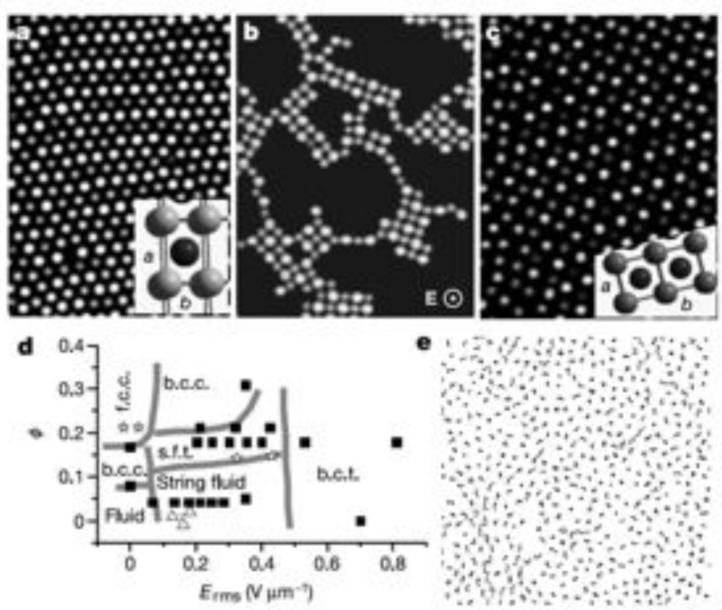


J. J. Crassous et al., Polymer (2015)

Template-driven self-assembly

- to create better defined or specifically oriented (epitaxial growth) structures
- to create well-defined 1D, 2D and 3D assemblies
- combination of top down and bottom up approaches

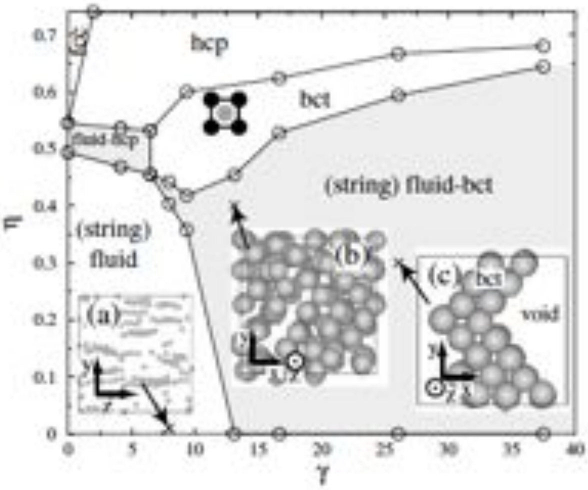
AC electric field driven SA



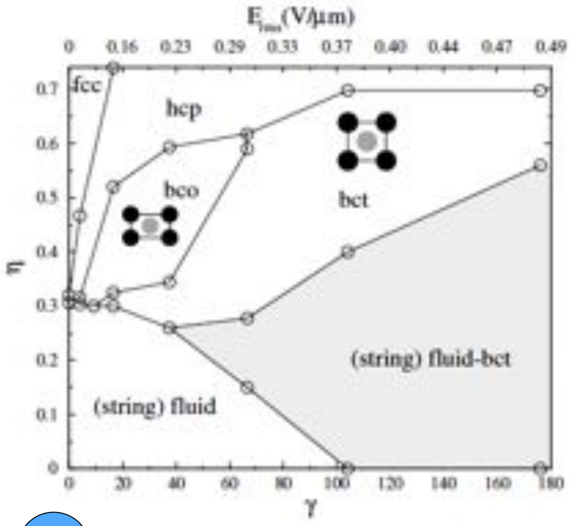
A. Yethiraj & A. van Blaaderen, Nature (2003)

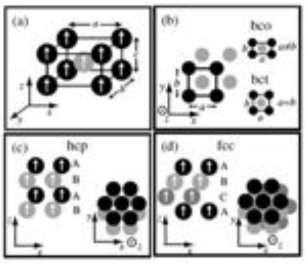
Self-assembly of dipolar particles

Dipolar hard spheres

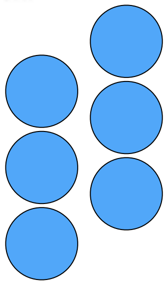


Dipolar soft spheres

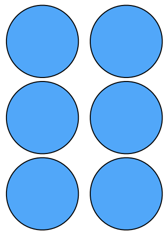




Hynninen & Dijkstra, Phys Rev Lett. (2005)



attractive

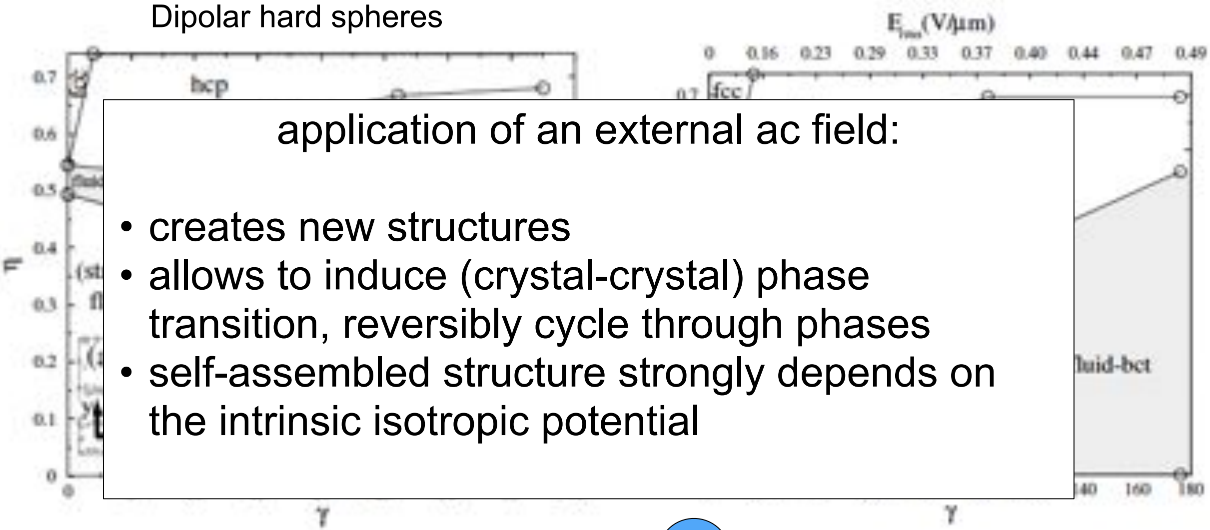


repulsive

Self-assembly of dipolar particles

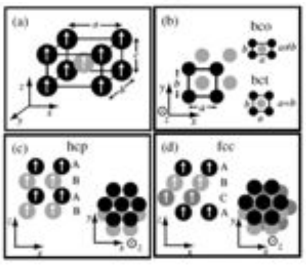
Dipolar soft spheres

Dipolar hard spheres

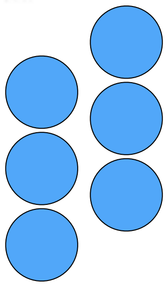


application of an external ac field:

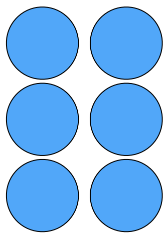
- creates new structures
- allows to induce (crystal-crystal) phase transition, reversibly cycle through phases
- self-assembled structure strongly depends on the intrinsic isotropic potential



Hynninen & Dijkstra, Phys Rev Lett. (2005)



attractive



repulsive

Hard vs soft dipolar particles

$$\beta u_{\mathrm{dip}}(\mathbf{r}_{ij}) = \frac{\gamma}{2}\left(\frac{\sigma}{r_{ij}}\right)^3 (1 - 3\cos^2\theta_{ij}),$$

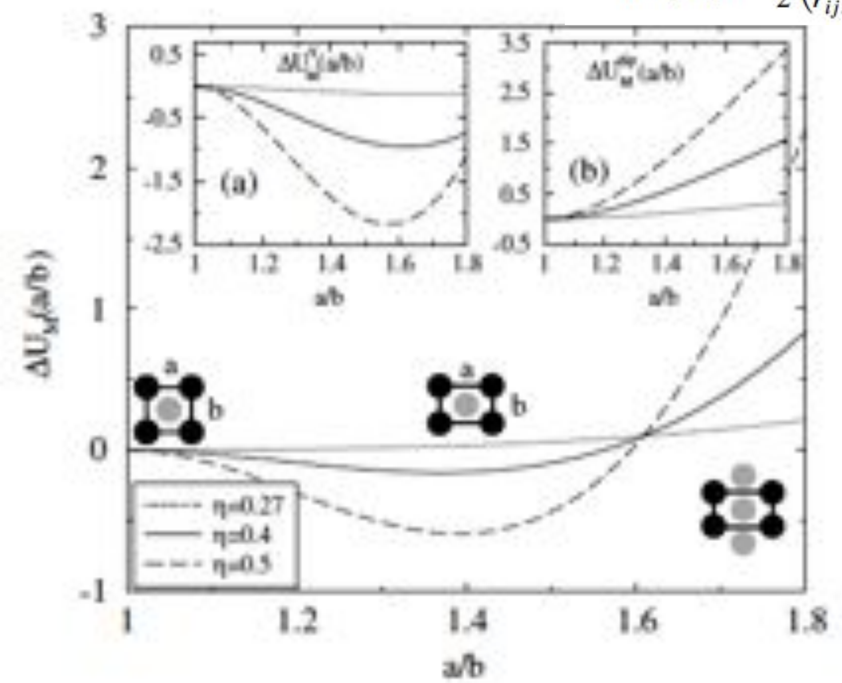
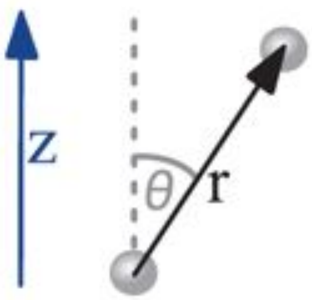


FIG. 4. Change in the Madelung energy $\Delta U_{\mathrm{M}}(a/b) = U_{\mathrm{M}}(a/b) - U_{\mathrm{M}}(1)$ of a bco crystal when a/b is increased from one. The results are for dipolar soft spheres with $\kappa\sigma = 10.0$, $\epsilon = 12.54$, and $\gamma = 37.5$, at packing fractions $\eta = 0.27$, 0.4, and 0.5. The insets (a) and (b) show the soft and dipolar parts of the Madelung energy change, respectively.

Hynninen & Dijkstra,
Phys Rev Lett. (2005)

Self-assembly of dipolar spheres



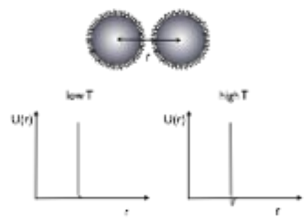
$$V(\mathbf{r}) \equiv \epsilon[\phi_{\mathrm{I}}(r) + \xi\phi_{\mathrm{A}}(r)P_2(\cos\,\theta)]$$

isotropic potential

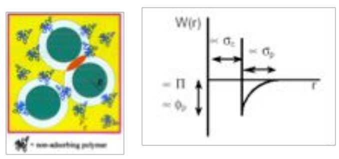
dipolar contribution

possible contributions to the isotropic potential

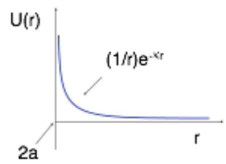
hard sphere, sticky sphere



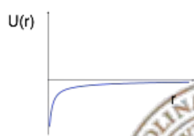
depletion interaction



screened Coulomb (Yukawa)



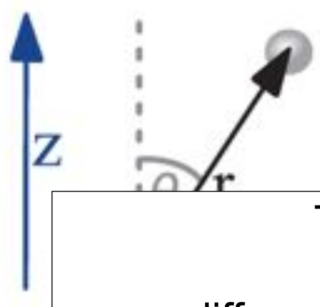
van der Waals



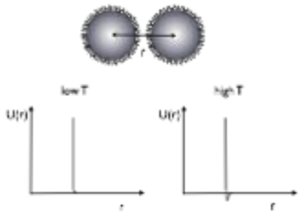
…

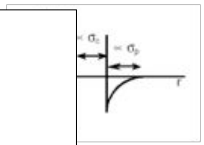
Self-assembly of dipolar spheres

possible contributions to the isotropic potential



hard sphere, sticky sphere





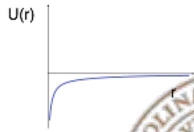
Tuneable total potential:

- very different length scales
- strength strongly dependent on particle properties

$V(\mathbf{r}) = \epsilon[\phi$

isotropic potential

van der Waals

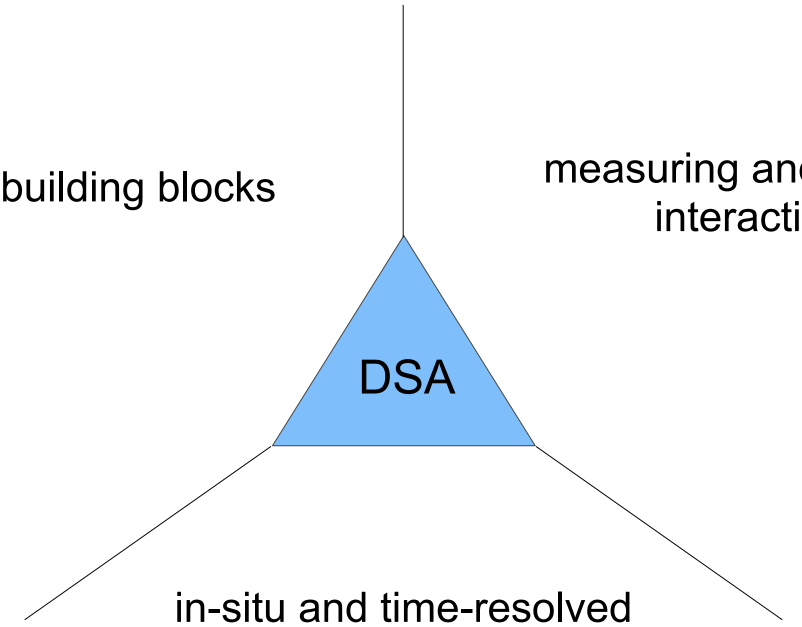


…

Field-driven self-assembly - key ingredients

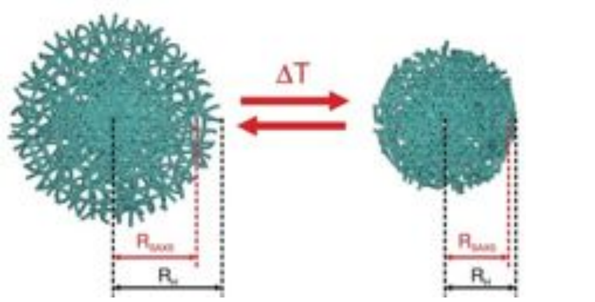
optimised building blocks

measuring and tailoring interactions



in-situ and time-resolved characterisation of forming structures

Thermoresponsive microgels as building blocks for DSA

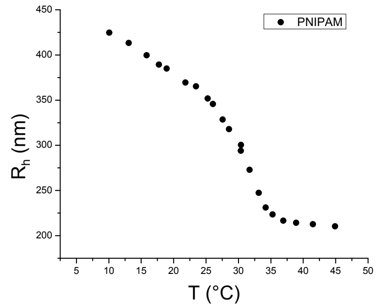


good solvent
=> swollen

$T_c \approx 33^oC$

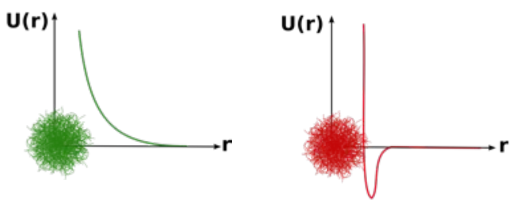
poor solvent
=> collapsed

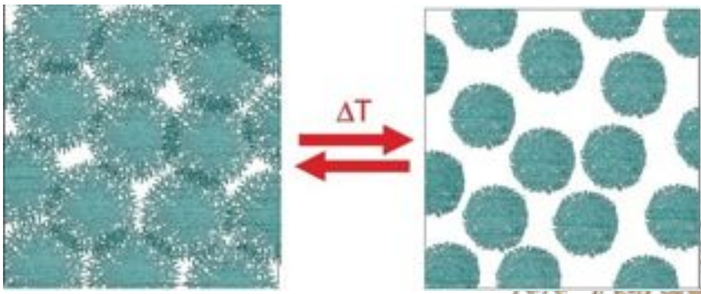
poly(N-isopropylacrylamide)



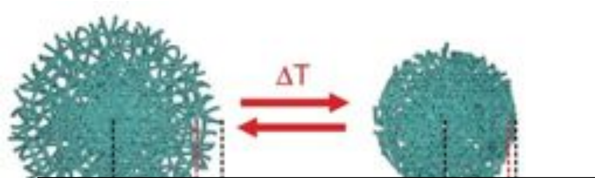
T < VPT

T > VPT

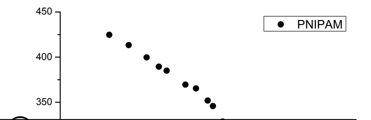




Thermoresponsive microgels as building blocks for DSA



poly(N-isopropylacrylamide)

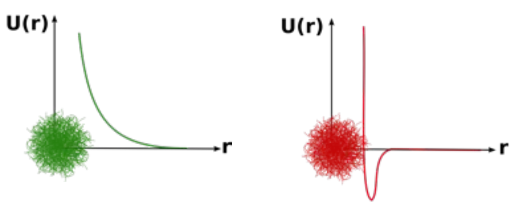


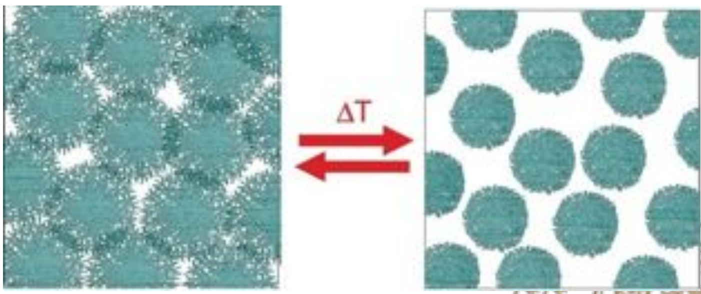
microgels are ideal building blocks because

- externally tuneable volume fraction → trigger phase transition, annealing mechanism

T < VPT

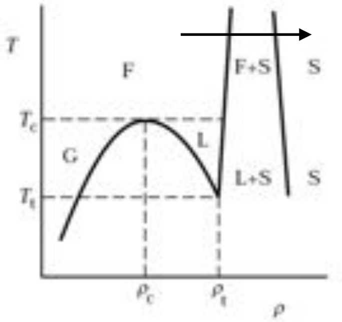
T > VPT





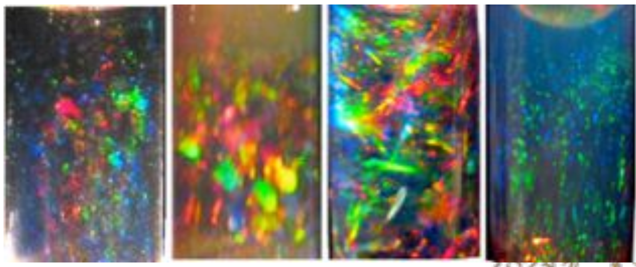
In-situ variation of the effective volume fraction

Phase diagram of generic atomic system

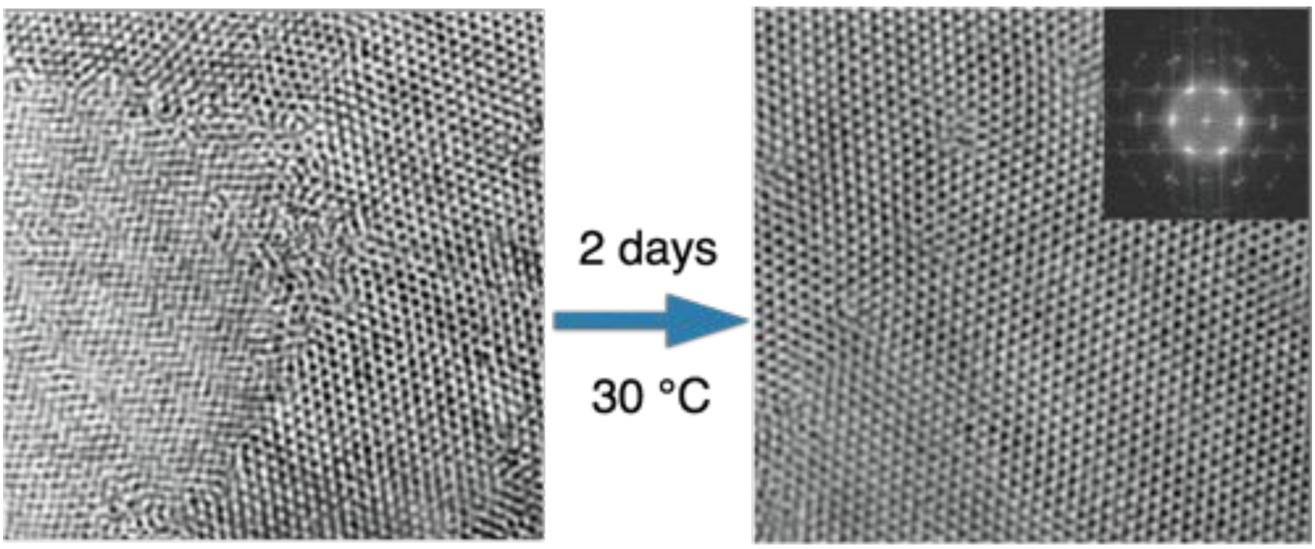


use T-jump to increase packing fraction

21°C   making artificial opals

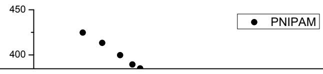


Thermal annealing



Thermoresponsive microgels as building blocks for DSA

poly(N-isopropylacrylamide)



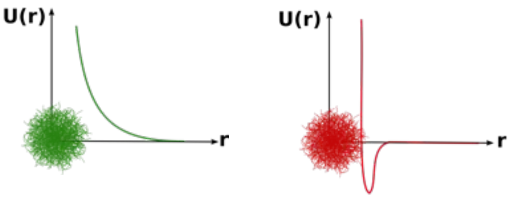
microgels are ideal building blocks because

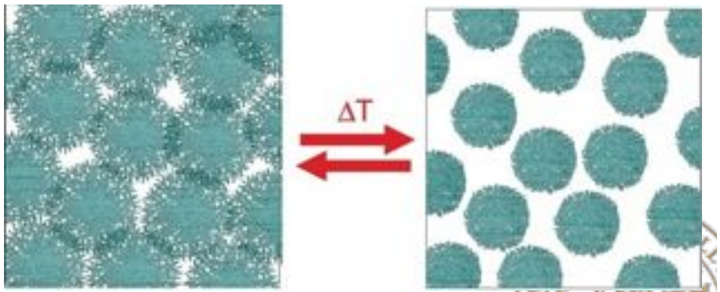
- externally tuneable volume fraction → trigger phase transition, annealing mechanism
- can be made into different shapes

good
=> sw

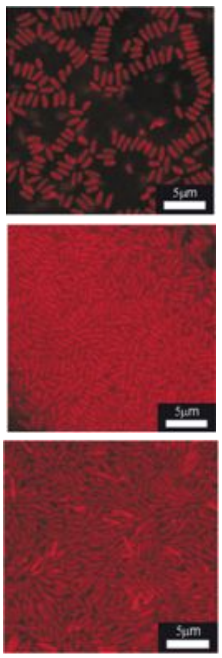
T < VPT

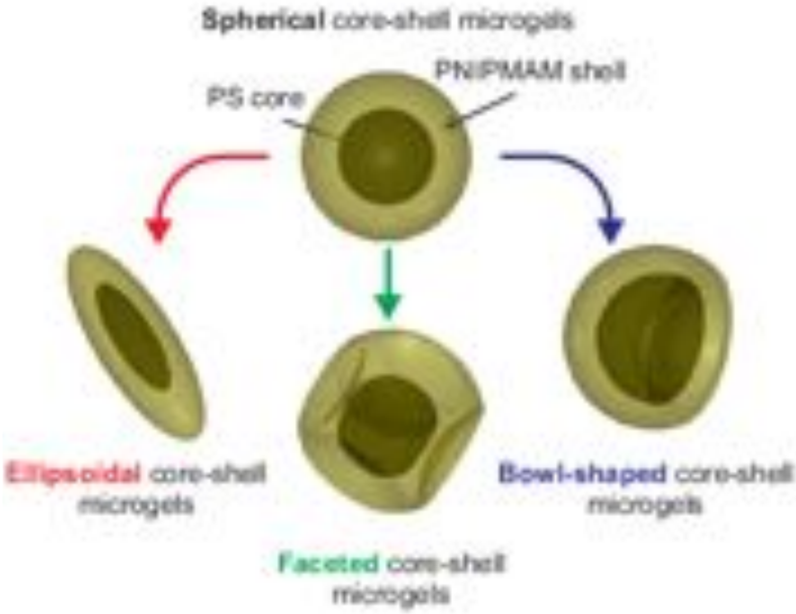
T > VPT

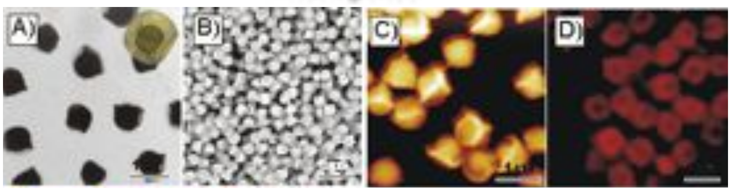


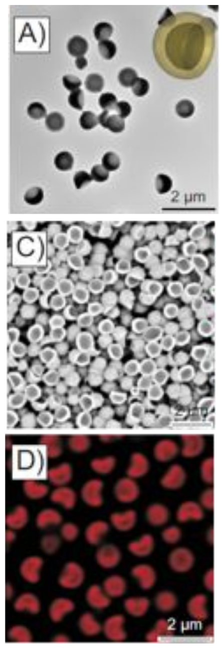


Engineering particle shape for new DSA building blocks

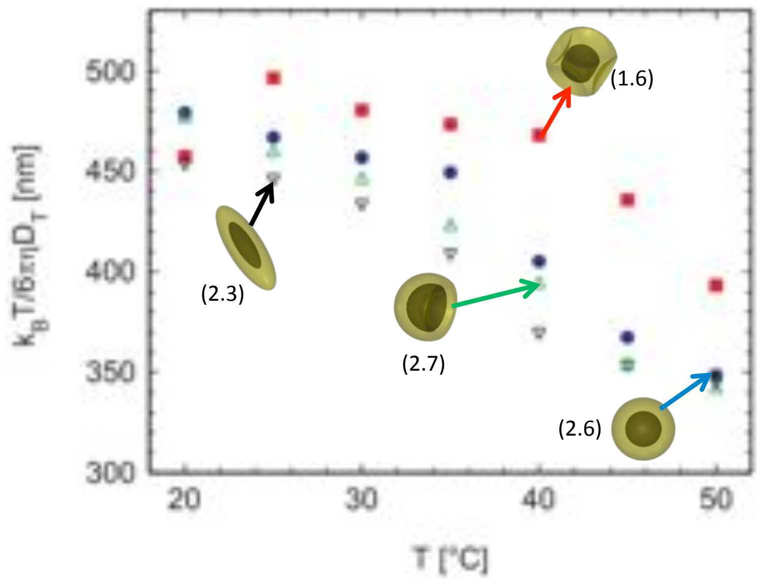






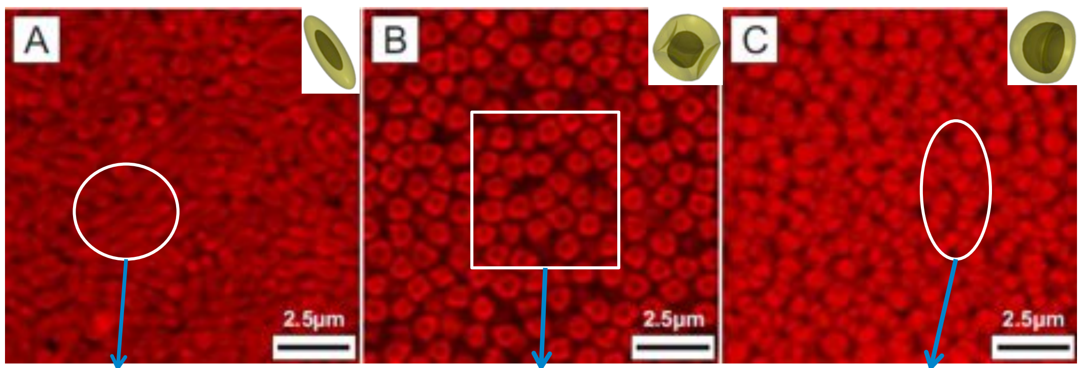


Anisotropic particles maintain thermoresponsive nature



Shape and jamming

Jammed Dispersions (20°C; Samples prepared by centrifugation by removing the excess supernatant)



Local nematic order

Formation of larger voids (defects)

Stack formation worm-like structures (local order)

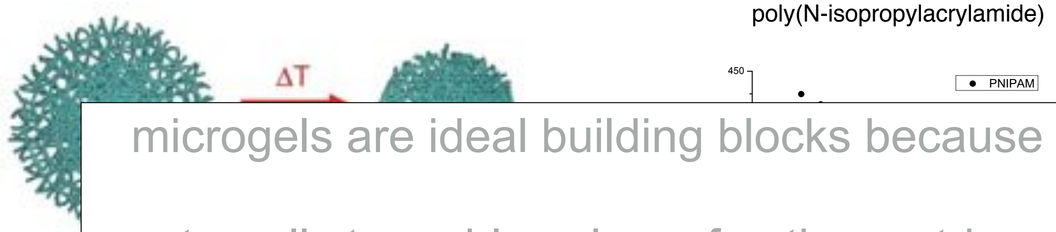
→ **Shape Matters** → Earlier jamming then or

Δ T

Change of anisotropy/angularity/shape/interactions

Thermoresponsive microgels as building blocks for DSA

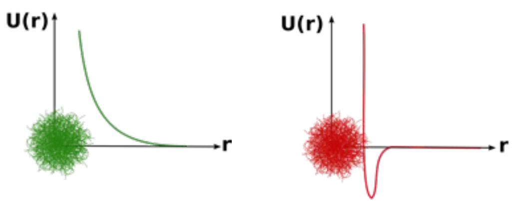
poly(N-isopropylacrylamide)

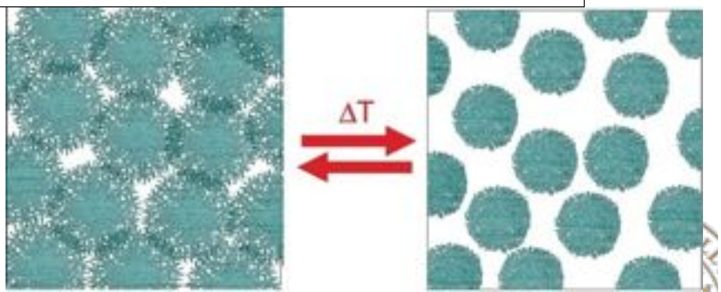


good s
=> sw

microgels are ideal building blocks because

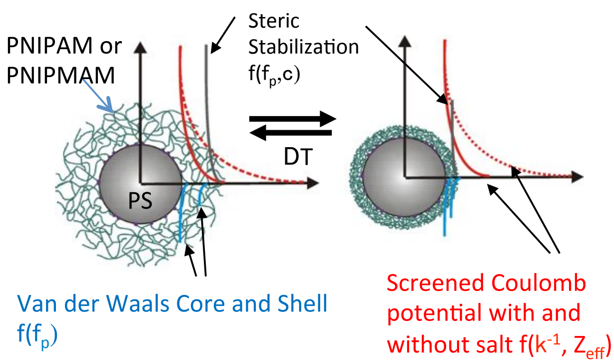
- externally tuneable volume fraction → trigger phase transition, annealing mechanism
- can be made into different shapes
- externally tuneable interaction potential

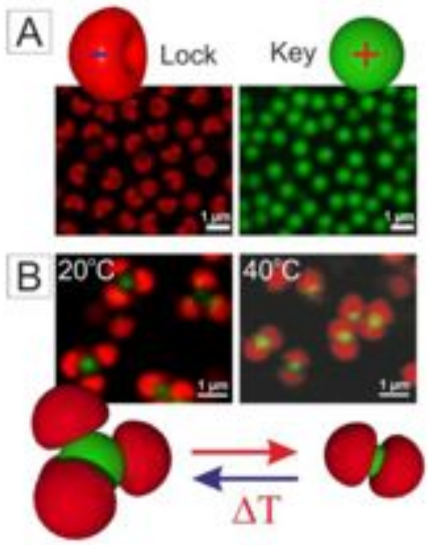




Tuning interparticle potentials

building reconfigurable molecules





Crassous et al, Langmuir, 2006

Thermoresponsive microgels as building blocks for DSA

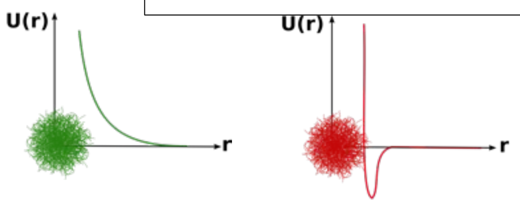
microgels are ideal building blocks because

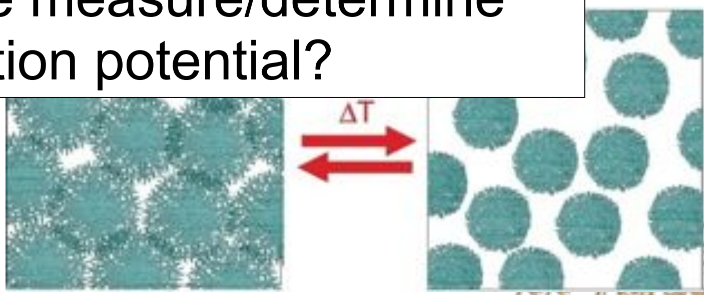
- externally tuneable volume fraction → trigger phase transition, annealing mechanism
- can be made into different shapes
- externally tuneable interaction potential

But how do we measure/determine interaction potential?

good
=> sw

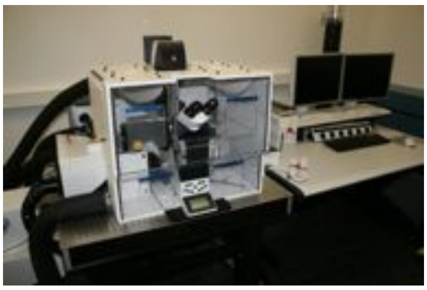
T < VP

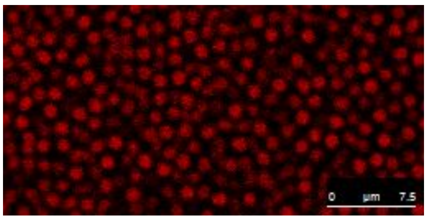


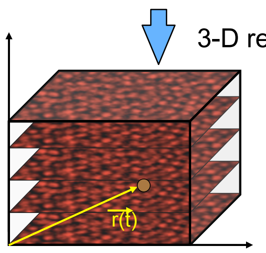


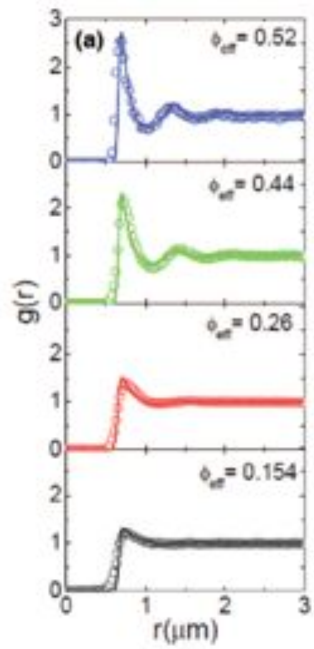
Characterising interparticle interactions in real space

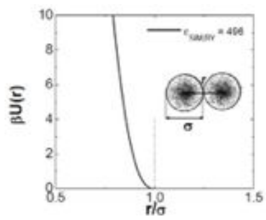
confocal laser scanning microscopy (CLSM)









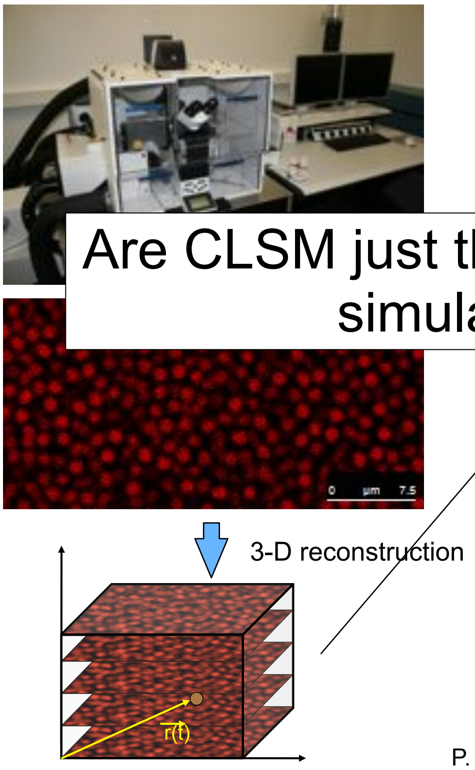


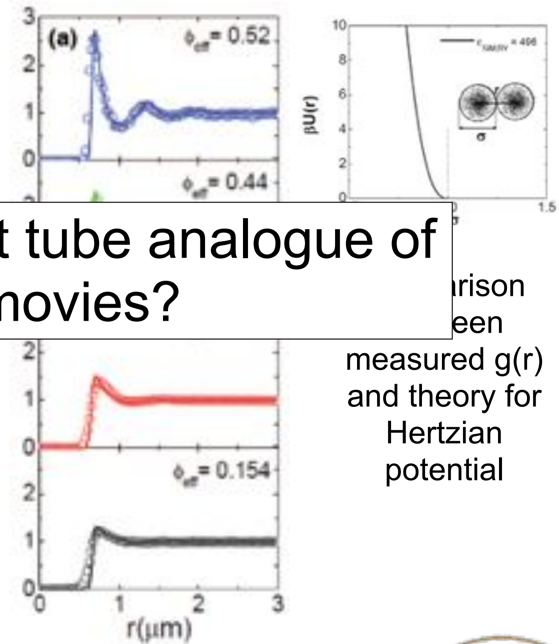
comparison between measured g(r) and theory for Hertzian potential

P. S. Mohanty et al., J. Chem. Phys. (2014)

Characterising interparticle interactions in real space

confocal laser scanning microscopy (CLSM)



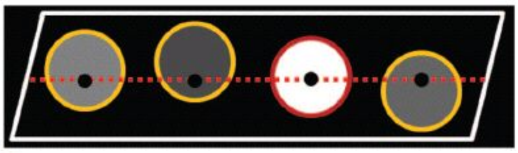


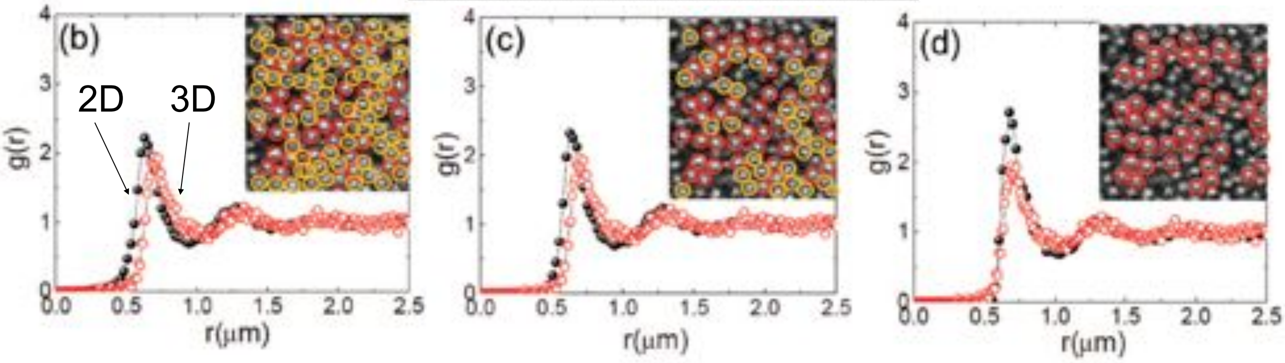
...rison ...een measured g(r) and theory for Hertzian potential

P. S. Mohanty et al., J. Chem. Phys. (2014)

Technical interlude: comparing CLSM and simulations

Comparing g(r) in 2D and 3D



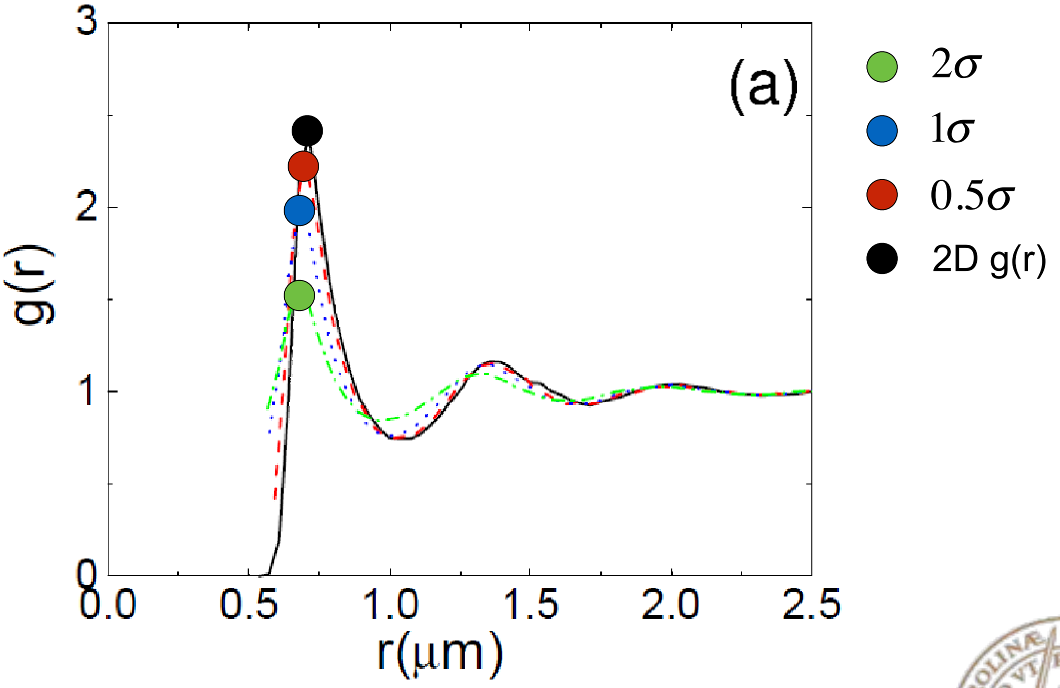


Problem: Different optical resolution in xy and z

P. S. Mohanty et al., J. Chem. Phys. (2014)

Technical interlude: comparing CLSM and simulations

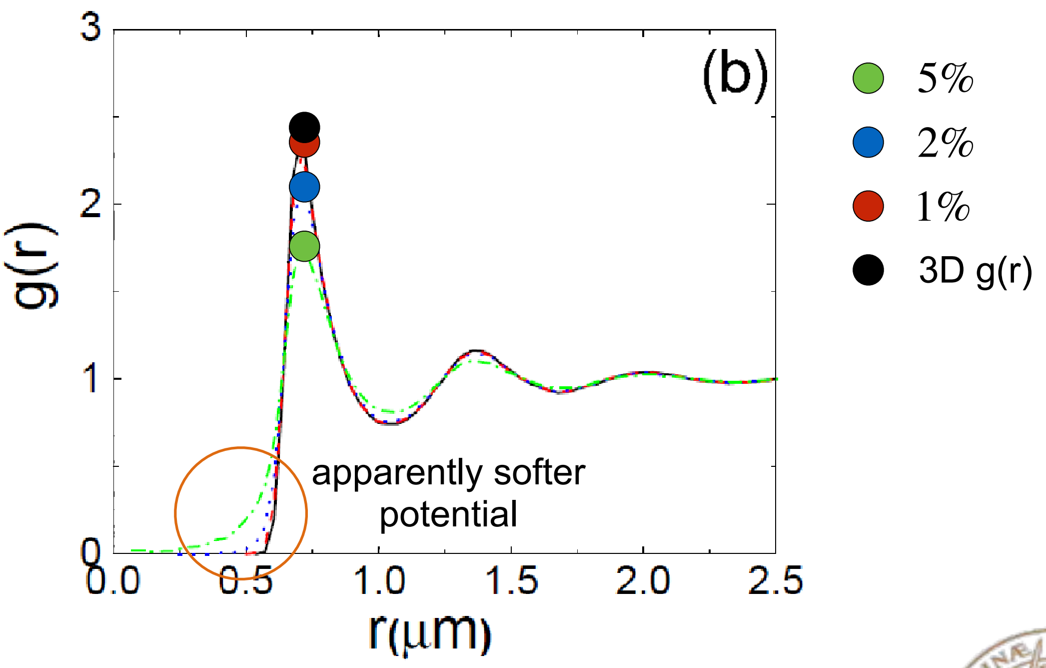
Effect of effect of out-of-plane particles for 2D g(r)



P. S. Mohanty et al., J. Chem. Phys. (2014)

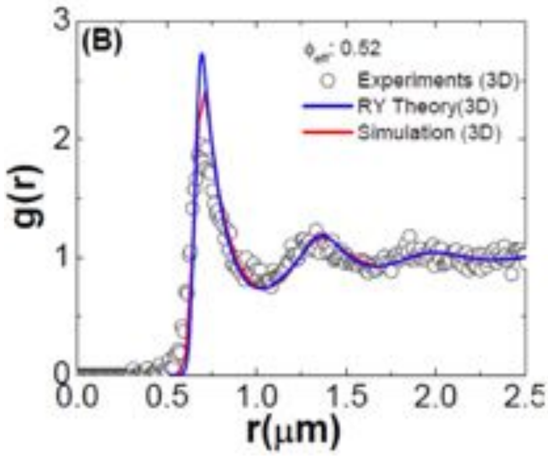
Technical interlude: comparing CLSM and simulations

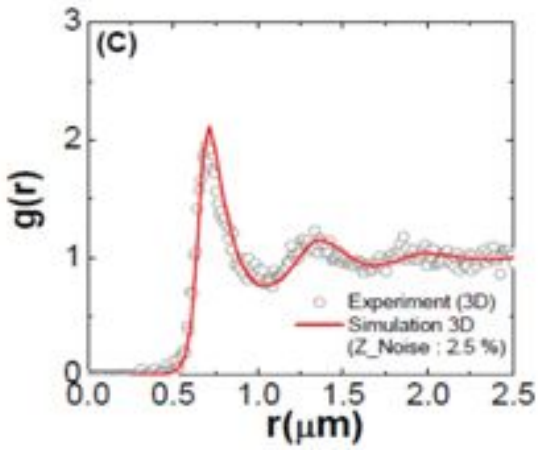
Effect of effect of z-noise for 3D g(r)



P. S. Mohanty et al., J. Chem. Phys. (2014)

Technical interlude: comparing CLSM and simulations

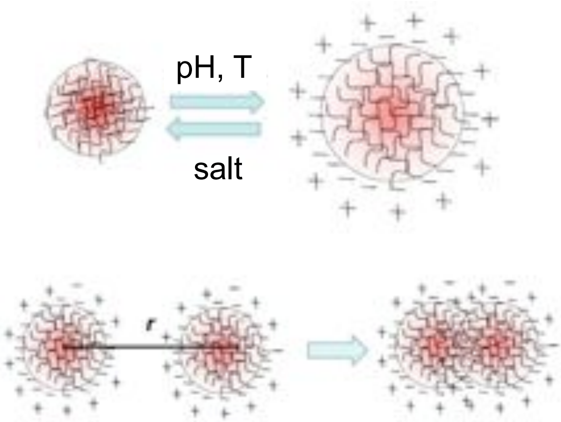




Also finite scan speed, important for highly diffusive systems

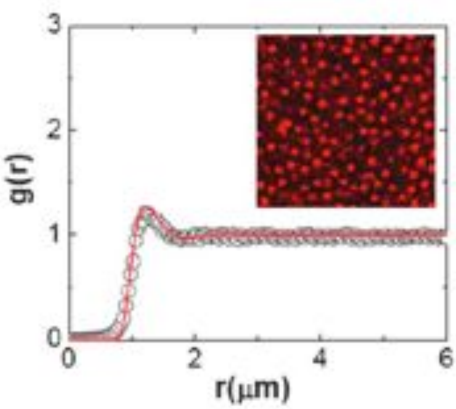
P. S. Mohanty et al., J. Chem. Phys. (2014)

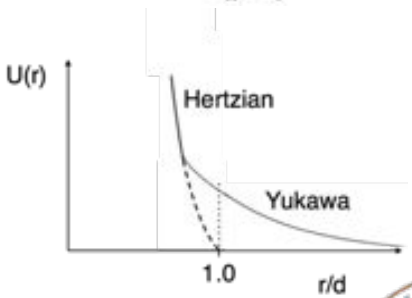
Ionic microgels as soft dipolar particles



long-range Yukawa short-range soft

(similar to "dusty plasma")

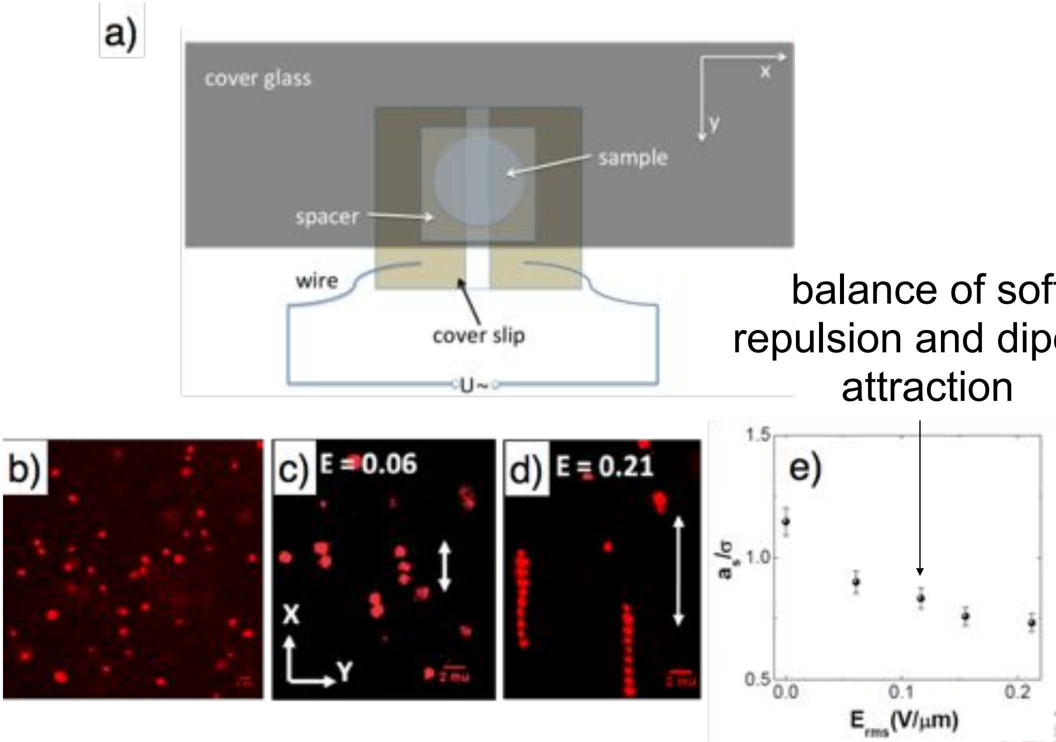




J. Riest, P.S. Mohanty, P.S., C. Likos, Z. Phys. (2012)

P. S. Mohanty et al., Soft Matter (2012)

Adding an external homogeneous ac electric field

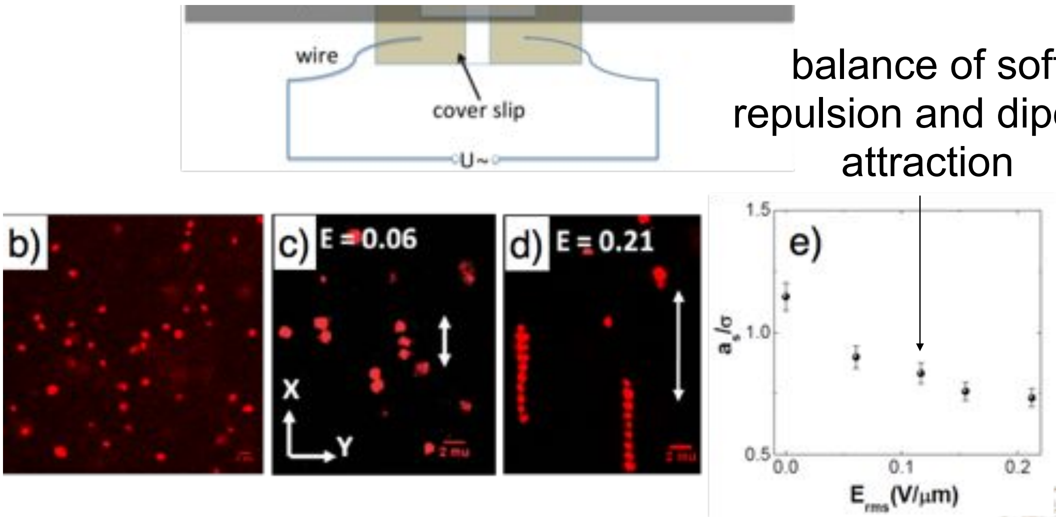


balance of soft repulsion and dipolar attraction

P. S. Mohanty et al., Soft Matter (2012)

Adding an external homogeneous ac electric field

but was is the strength of the dipolar attraction?



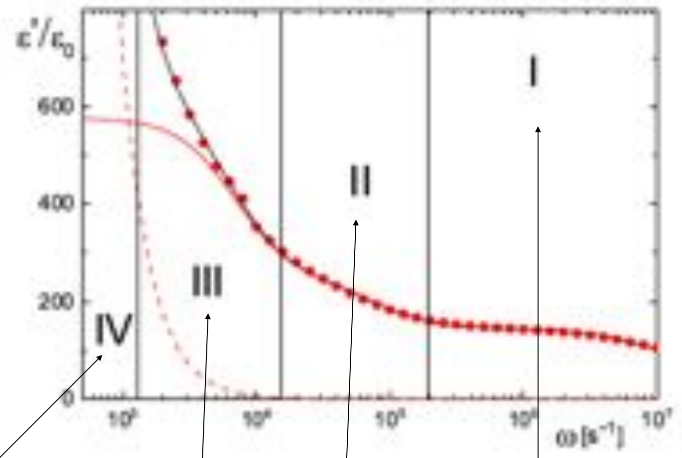
balance of soft repulsion and dipolar attraction

P. S. Mohanty et al., Soft Matter (2012)

Polarisability of ionic microgels

$$U_{dip}(\boldsymbol{R}) = -\frac{4\pi\epsilon_0\epsilon_f\alpha^2 a^6 \boldsymbol{E}_0^2}{R^3}\left[\frac{3cos^2\theta - 1}{2}\right]$$

insight from dielectric spectroscopy



$$\begin{aligned}\epsilon'_{exp} &= \epsilon' - \sigma''/\omega \\ \epsilon''_{exp} &= \epsilon'' + \sigma'/\omega\end{aligned}$$

conductivity contribution

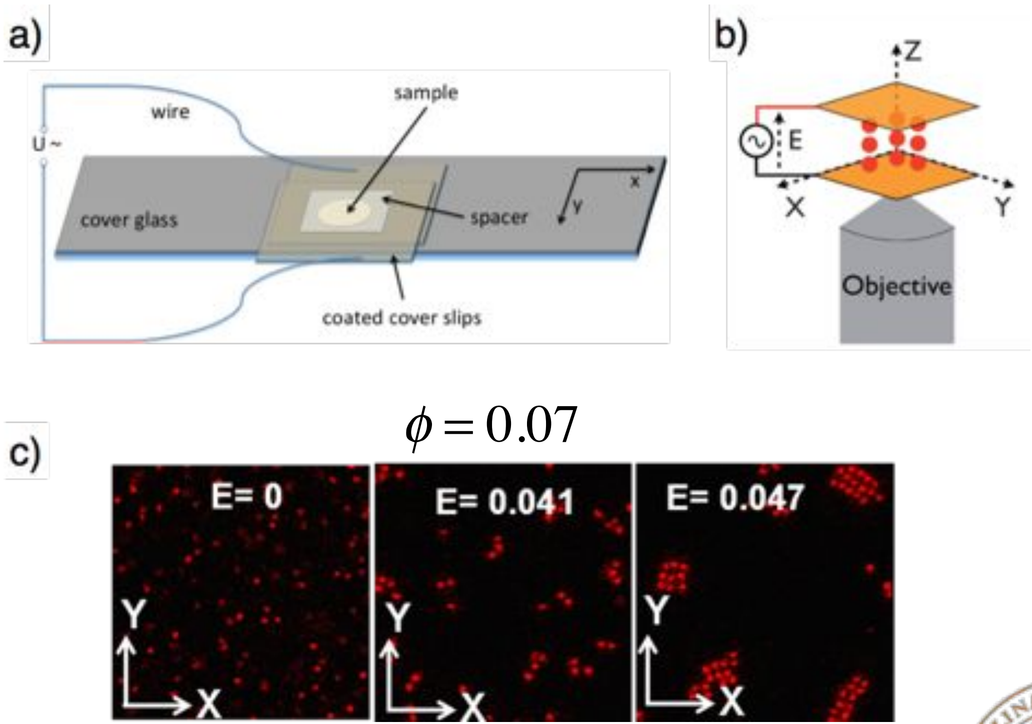
electrode polarisation dominates, depends strongly on gap width

diffuse electric double layer

mobile ions within microgel

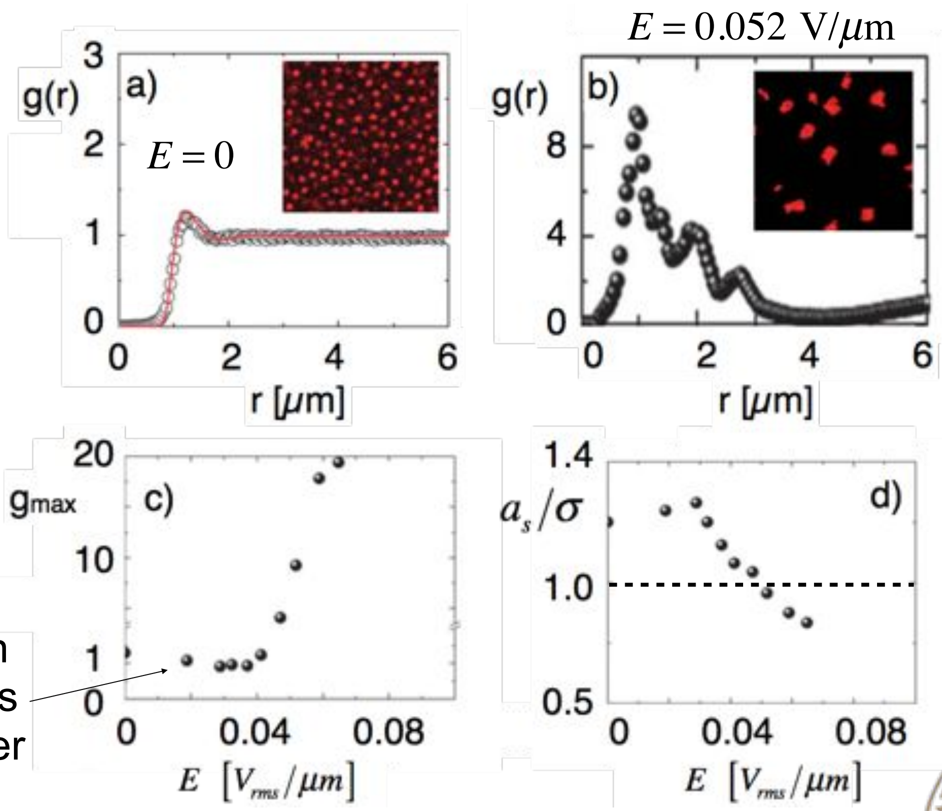
polarisation of the polymer backbone

Watching dipolar chains assemble



S. Nöjd et al., Soft Matter (2013)

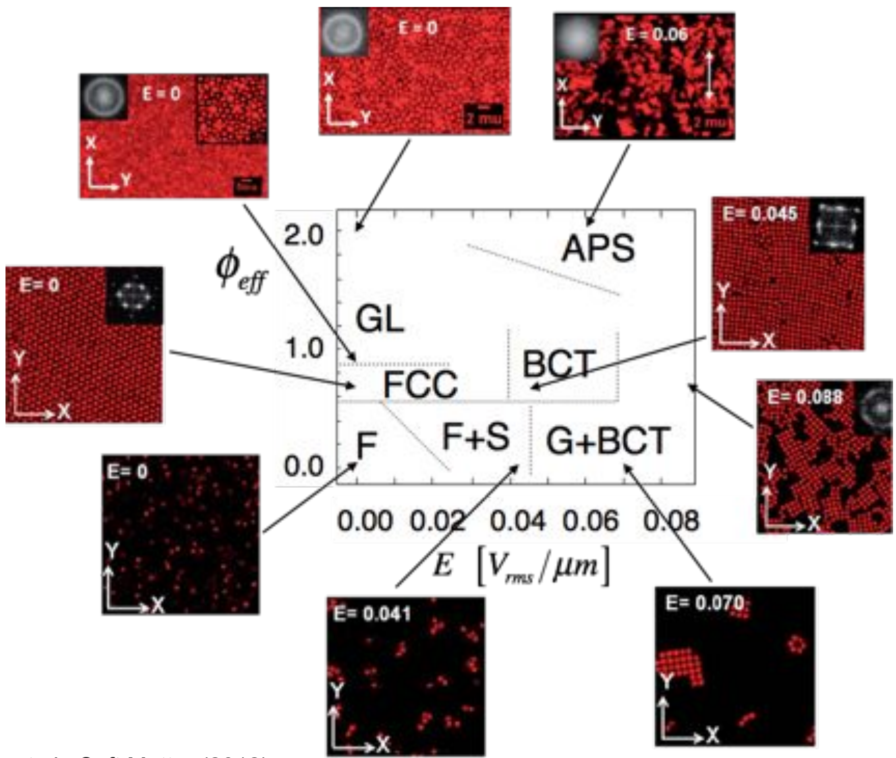
Analysing string cluster formation



string formation decreases 2D number density

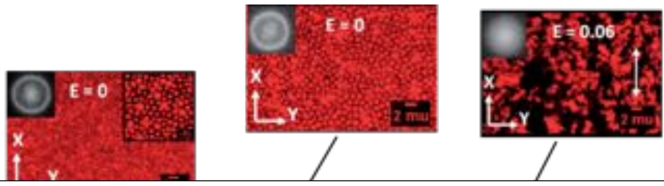
S. Nöjd et al., Soft Matter (2013)

SA at higher effective volume fractions



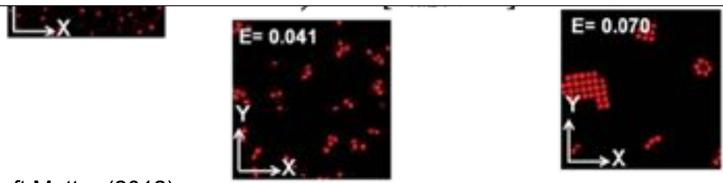
P. S. Mohanty et al., Soft Matter (2012)
S. Nöjd et al., Soft Matter (2013)

SA at higher effective volume fractions



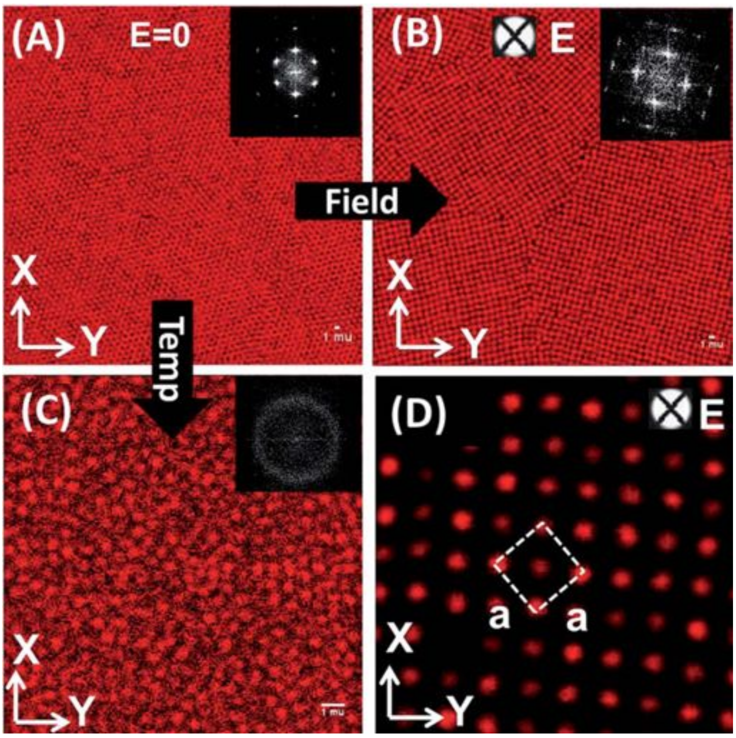
Summary:

- rich phase (state) diagram with among other phenomena a glass-BCT or arrested phase separated state
- can trigger crystal-crystal phase transitions → can we learn about the underlying mechanisms?



P. S. Mohanty et al., Soft Matter (2012)
S. Nöjd et al., Soft Matter (2013)

temperature as an additional control parameter



S. Nöjd et al., Soft Matter (2013)
P. S. Mohanty et al., Soft Matter (2012)

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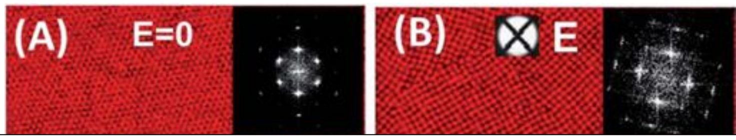
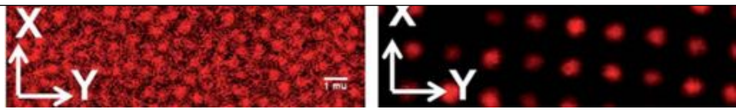


Summary:

can cycle through phase diagram along complex paths

but:

microgels are soft and easily deformable, how do we know that they don't change at high densities?



S. Nöjd et al., Soft Matter (2013)
P. S. Mohanty et al., Soft Matter (2012)

Technical interlude 2: How to investigate small changes in particles at ultra-high densities?

Problems of an experimentalist:

- lack of resolution in CLSM
- x-ray scattering: contribution from individual particle (form factor) and interparticle correlations (structure factor) convoluted

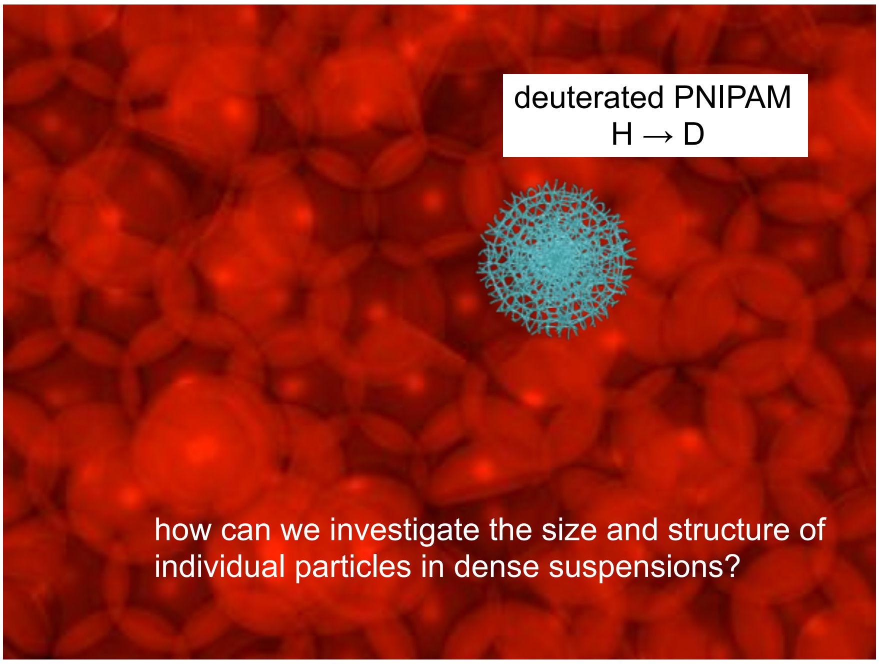
Solutions:

become a simulator

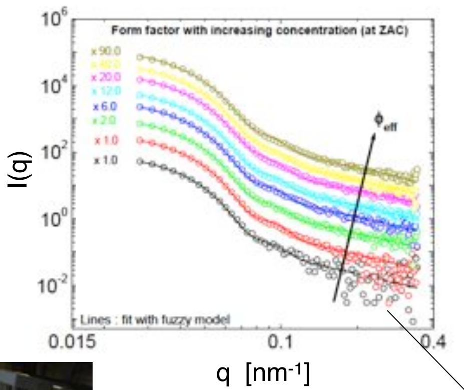
use neutrons

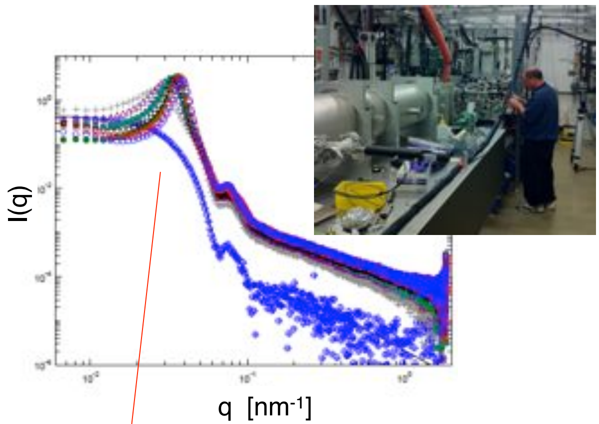
Contrast variation - or why neutrons

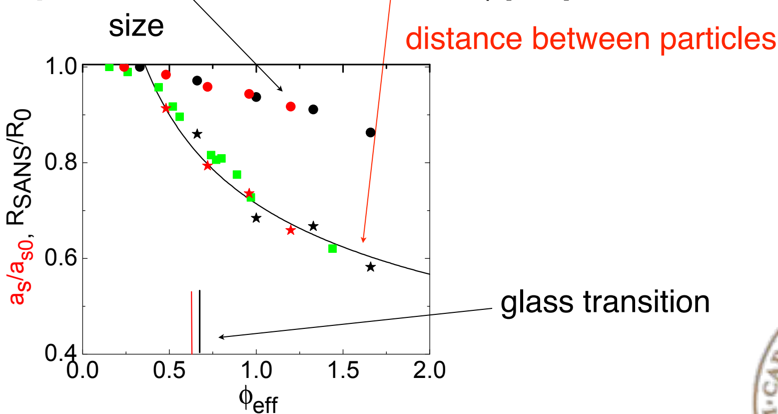
microgels at high densities



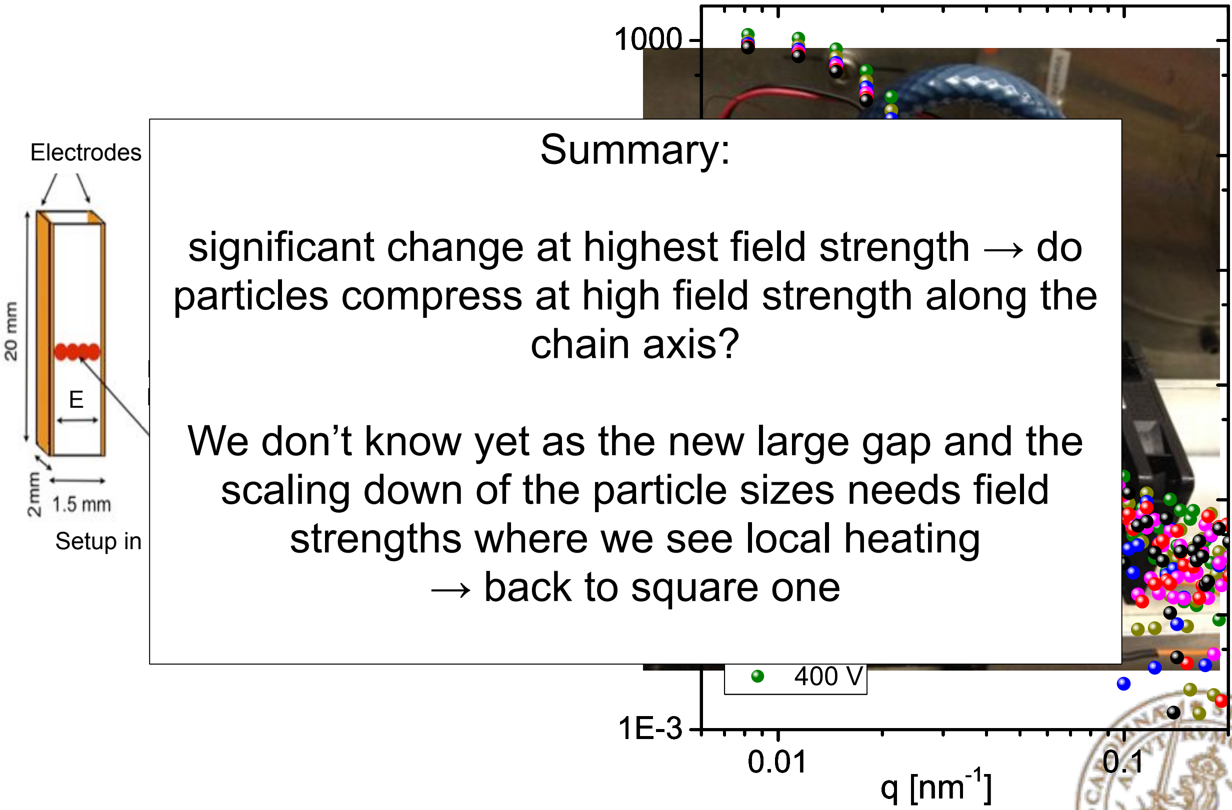
Combining SANS and SAXS: Shape and interactions







Can we do the same for particles in external fields?

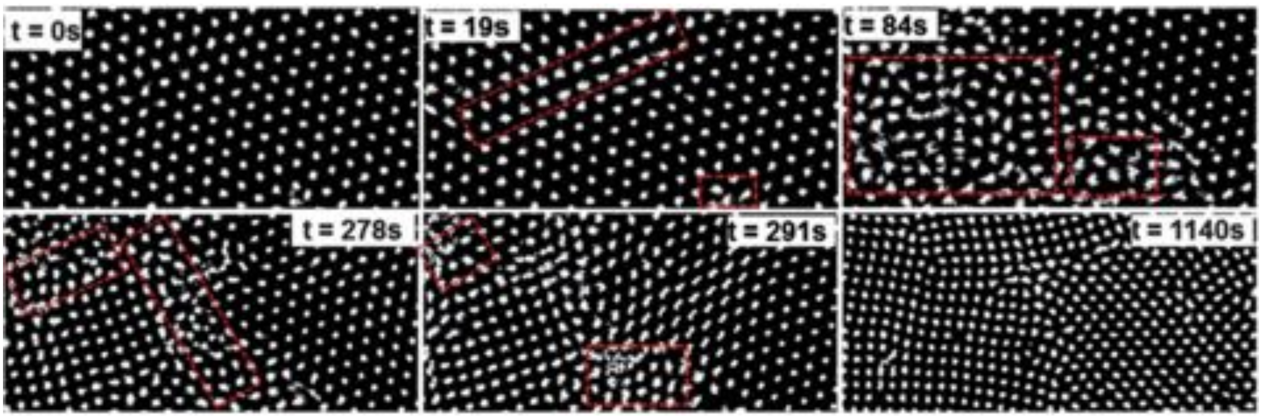


Summary:

significant change at highest field strength → do particles compress at high field strength along the chain axis?

We don’t know yet as the new large gap and the scaling down of the particle sizes needs field strengths where we see local heating → back to square one

Investigating phase transition kinetics and mechanisms



particle trajectories (mean square displacement) indicates local melting into diffusive fluid-like structure followed by re-crystallisation

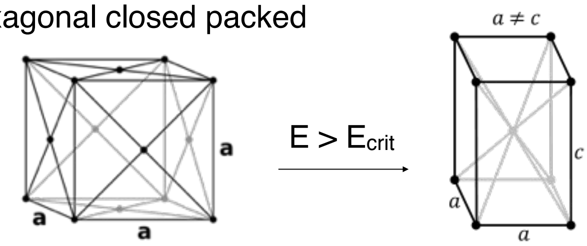
can we quantify this?

S. Nöjd et al., Soft Matter (2013)

Insight into solid-solid transitions

face-centered cubic
or
hexagonal closed packed

body-centered
tetragonal



$\phi = 1.36 \gg \phi_f$

bond order analysis

$$\Psi_s = \left| \frac{1}{N} \sum_{j=1}^{N} e^{si\theta_j} \right|$$

summation over N nearest neighbours, s = 4 or 6

→ population fractions

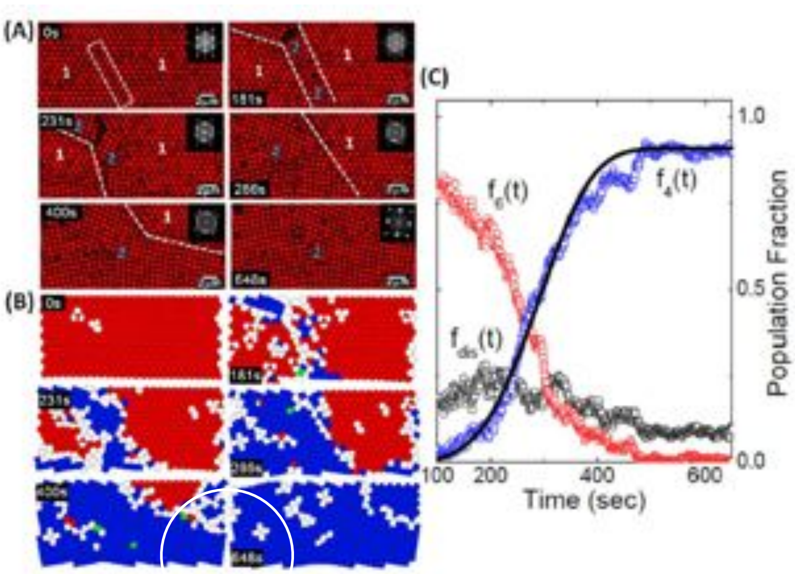
$f_6 : \Psi_6 > 0.7$

$f_4 : \Psi_4 > 0.55$

$f_{dis} : \Psi_6 < 0.7 \text{ and } \Psi_4 < 0.55$

P. S. Mohanty et al., PRX (2015)

Insight into solid-solid transitions



Avrami eqn.

$f_4 \sim (1 - \exp(-Kt^{\alpha}))$

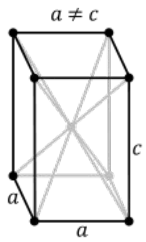
$\alpha = 4.0$

Transition through intermediate melting, nucleation and growth

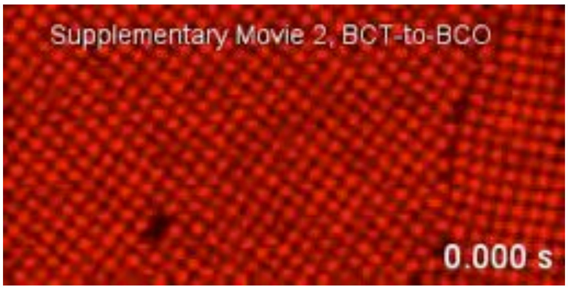
P. S. Mohanty et al., PRX (2015)

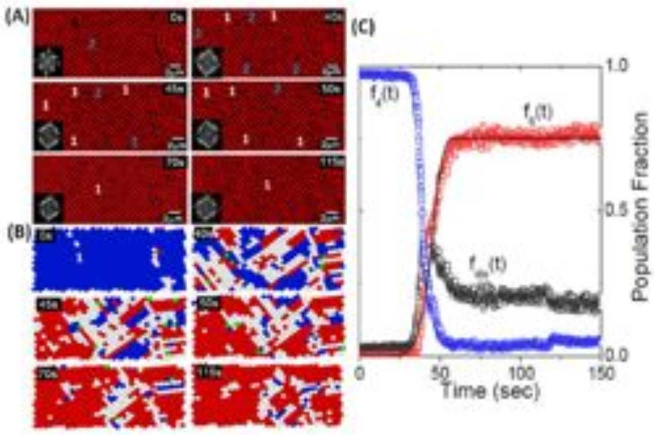
Insight into solid-solid transitions - reverse transition

body-centered
tetragonal



E = 0





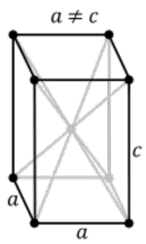
Diffusion-less martensitic transition,
long-lived metastable state

P. S. Mohanty et al., PRX (2015)

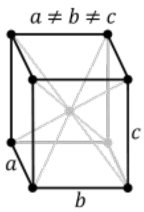
Insight into solid-solid transitions - reverse transition

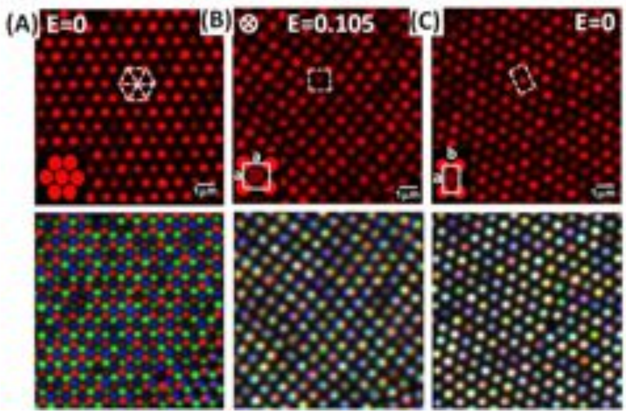
body-centered
tetragonal

body-centered
orthogonal



E = 0





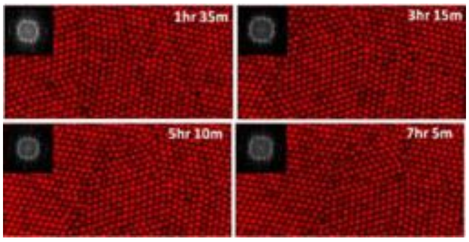
same system shows diffusive and
martensitic solid-solid transition

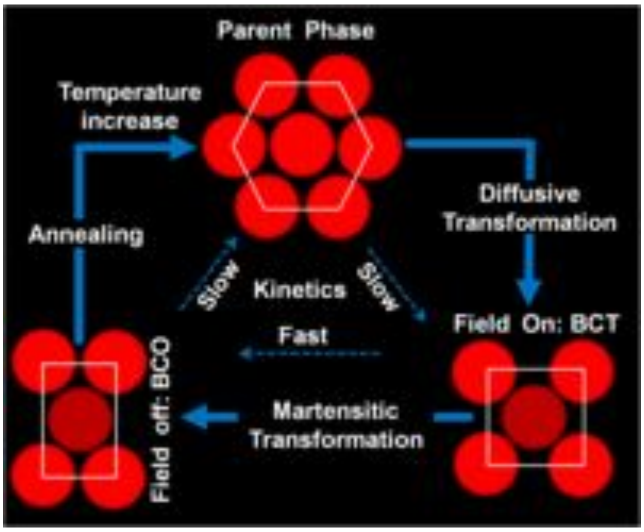
long-lived metastable state

P. S. Mohanty et al., PRX (2015)

Path-dependent solid-solid transitions

after field has been
turned off: bco





but for $\phi = 0.43 < \phi_f$
after field has been
turned off: bco → fluid

P. S. Mohanty et al., PRX (2015)